Current and future risks of radionuclide contamination to New Zealand's food supply.

A thesis submitted in fulfilment

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by

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Abstract

Identifying current and future food contamination risks is an important component of ensuring food security. Exposure to ionising radiation through dietary intake of radionuclides poses a potential source of food safety concern to New Zealand. Identifying and addressing current levels of exposure and future sources is necessary to ensure food security.

An analytical survey of 40 common foods in the New Zealand diet was undertaken to establish current ranges for important radionuclides, including those of anthropogenic and natural origin. The derived activity concentrations for the thirteen radionuclides analysed were used to undertake dietary exposure modelling for ionising radiation doses to different age and gender groups of the New Zealand population. Exposure to naturally occurring radionuclides, in particular polonium-210, is the predominant source of the dose to the population, with seafood in the diet being the primary contributor to this dose. Anthropogenic radionuclides in contrast are present at only trace activity concentrations and present a low dietary exposure to ionising radiation dose.

Exposure to caesium-137 and polonium-210 through seafood was identified as a source of near-term risk to increase the dietary burden to ionising radiation. Seafood samples from different species and harvested from different coastal regions were surveyed to determine the variability in activity concentrations. Activity concentrations of caesium-137 were low and showed little variation between regions. However, polonium-210 activities in shellfish were significantly higher than in other seafood types and displayed large variation between species. A dietary exposure model for seafood consumers identified the short-term risks from anthropogenic radionuclide exposure through seafood as a result of oceanic transport of caesium-137 are minimal in comparison to the dose of natural polonium-210 in these foods.

The agricultural use of phosphate fertilisers containing radium-226 impurities was examined as a potential source for a long-term increase to the dietary ionising radiation burden. Analysis of phosphate ore and fertiliser samples identified a range of radium-226 activity concentrations. Radium-226 activity concentrations in agricultural soils, and also unexpectedly radium-228, appear to have increased considerably against values reported in the 1970s. Soil partitioning results showed that the radium-226 is predominantly bound in non-labile fractions and is unlikely to be available for crop uptake.

Crop uptake in a number of common agricultural and horticultural crops was analysed to establish the dietary implications of an increase in soil radium-226 activity concentrations. The calculated concentration ratios correlate well with international default values for estimating crop uptake. Analysis of the concentration ratio in foliage at a site with a gradient of soil radium-226 established no increase in the crop activity concentration occurred. As a result, long-term loading of soil with radium-226 is unlikely to present a dietary risk. This conclusion was confirmed through conservative forecasting of the increased dose of radium-226 that might occur at current soil loading rates based on current fertiliser activity concentrations. The forecast model calculated that the increase to dietary ionising radiation burden is unlikely to reach thresholds requiring regulatory intervention for close to two millennia.

Both short- and long-term radiological risks to New Zealand food security are considered minimal. New Zealand is currently well insulated from the risks of radiological exposure through the diet.

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This thesis is dedicated to the memory of my grandfather

William Arthur Brothers

(1929-2009)

You inspired me to be curious about the natural world

and not to be afraid to try my hand at anything.

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It is unlikely that the research in this thesis would have been conceived of if not for the data gaps raised following the nuclear disaster at Fukushima-Daiichi. For that reason it is important not to forget the massive loss of life, upheaval and hardship that have resulted from the 2011 Tōhoku earthquake and tsunami in Japan.

Glossary

Term	Description
Alpha decay (α)	Nuclear decay resulting in the release of a particle containing 2 protons and 2 neutrons (termed an alpha particle). The resulting nucleus is of an element reduced in atomic number by 2 and atomic mass by 4, e.g. Uranium-238 » Thorium-234.
Anthropogenic radionuclide	A radionuclide produced through human activities, this can include fission products for the nuclear fission process e.g. Strontium-90, activation products from neutron activation of elements e.g. Cobalt-60, and transuranic elements e.g. Americium-241.
Becquerel (Bq)	The unit for activity is the becquerel (Bq). One becquerel corresponds to one nuclear transformation per second. The becquerel is an SI unit and can include a metric prefix: millibecquerel (mBq) = 10^{-3}Bq kilobecquerel (kBq) = 10^{3}Bq megabecquerel (MBq) = 10^{6}Bq gigabecquerel (GBq) =10^{9}Bq terabecquerel (TBq) =10^{12}Bq tetabecquerel (PBq) =10^{15}Bq.
Beta-minus decay (β-)	Nuclear decay occurring as a neutron converts to a proton in the unstable nucleus, this results in the ejection of an electron (termed a beta particle) from the nucleus. The resulting nucleus is of an element increased in atomic number by 1 and unchanged in atomic mass, e.g. Strontium-90 » Yttrium-90.
Demersal	The area of a water body close to the bottom. Relating to fish, this is those species inhabiting the zone of water around the bottom.
Electron Capture (ec)	Nuclear decay occurring as an electron in the electron shell is captured by the nucleus resulting in conversion of a proton to a neutron. The decay is associated with release of gamma emissions as the nucleus releases excess energy. The resulting nucleus is of an element reduced in atomic number by 1 and unchanged in atomic mass, e.g Potassium-40 » Argon-40.
Gamma emission (γ)/ Isomeric Transition (Iγ)	Excess energy remaining in a nucleus following radioactive decay is released in the form of photons to return the nucleus to its ground state, a process termed isomeric transition. The photons are termed gamma emissions and are generally released instantaneously following a radioactive decay, exceptions where emission is delayed are termed metastable (denoted by m) e.g. Technetium-99m.

Term	Description
Half-life	The time required for the activity of a radionuclide to decrease, by a radioactive decay process, by half.
Inventory	The calculated total amount of radionuclide activity in a certain area.
Isotope	Categorisation of nuclides with the same atomic number but with different atomic masses.
Marinelli beaker	A beaker utilised in gamma spectroscopy that cylindrically surrounds the detector allowing for greater detection efficiency.
Minimum Detectable Concentration (MDC)	The lowest measurement where there is a level of confidence of 95%, that a radionuclide's activity will be detected.
Naturally Occurring Radioactive Material (NORM)	A term referencing any radionuclide that is naturally present in the environment and at a level consistent with its normal environmental background.
Pelagic	The area of water consisting of the upper layers of the open sea. Relating to fish, this is those species inhabiting the upper layers of the open sea.
Primordial radionuclide	A radionuclide generated prior to the formation of the planet and due to its long half-life remains detectable in the environment to the present day. E.g. Potassium-40, Thorium-232 and Uranium-238.
Radionuclide	An elemental isotope that is unstable and will undergo nuclear decay to stabilise its nucleus
Sievert (Sv)	The unit for absorbed dose of ionising radiation. The sievert is an SI unit and can include a metric prefix: millisievert (mSv) = 10^{-3}Sv.
Spontaneous Fission (sf)	The rare natural nuclear fission of an unstable nucleus in the absence of neutron induction.
Technologically Enhanced Naturally Occurring Radioactive Material (TeNORM)	A term referencing a naturally occurring radioactive material that through human activities, such as mining, filtering or concentrating production streams; becomes elevated above the natural background in the environment.

Abbreviations

Abbreviation	Full term
Bq	Becquerel
CEC	Cation exchange coefficient
dw	Dry weight
EEZ	Exclusive Economic Zone
FMA	Fishery Management Area
HPGe	High Purity Germanium
IAEA	International Atomic Energy Agency
ICRP	International Commission on Radiological Protection
kBq	kilobecquerel
LB	Lower Bound
MBq	megabequerel
mBq	millibecquerel
MDC	Minimum Detectable Concentration
MHLW	Japanese Ministry of Health, Labour and Welfare
mSv	millisievert
nSv	nanosievert
NORM	Naturally Occurring Radioactive Material
PBq	petabecquerel
RSD	Relative Standard Deviation
SD	Standard Deviation
Sv	Sievert
TBq	terabecquerel
TeNORM	Technologically Enhanced Naturally Occurring Radioactive Material
UB	Upper Bound
UN	United Nations
UNSCEAR	United Nations Scientific Committee on the Effects of Atomic Radiation
ww	Wet weight
Modes of radioactive decay	
α	Alpha decay
β-	Beta negative decay
ϵ	Electron capture decay
Iγ	Isomeric transition
sf	Spontaneous fission
γ	Gamma emission

Isotope data table

Isotope	Half life*	Decay route(s) (branching fraction %)	Principal emission energies (MeV)
Hydrogen-3 (^{3}H)	12.32 y	β^- to ^{3}He	β^-: 0.02
Beryllium-7 (^{7}Be)	53.29 d	ϵ to ^{7}Li	γ: 0.48
Carbon-14 (^{14}C)	5730 y	β^- to ^{14}N	β^-: 0.2
Potassium-40 (^{40}K)	1.3 x10^{8} y	β^- to ^{40}Ca (89%); ϵ to ^{40}Ar (11%)	β^-: 0.56 γ: 1.46
Cobalt-60 (^{60}Co)	5.27 y	β^- to ^{60}Ni	γ: 1.17;1.33
Rubidium-87 (^{87}Rb)	4.8 x10^{10} y	β^- to ^{87}Sr	β^-: 0.3
Yttrium-90 (^{90}Y)	2.7 d	β^- to ^{90}Zr	β^-: 2.3
Strontium-90 (^{90}Sr)	28.8 y	β^- to ^{90}Y	β^-: 0.5
Zirconium-95 (^{95}Zr)	64 d	β^- to ^{95}Ni	β^-: 0.4 γ: 0.72;0.75
Technetium-99 (^{99}Tc)	2.1 x 10^{5} y	β^- to ^{99}Ru	β^-: 0.3
Technetium-99m (^{99m}Tc)	6.0 h	Iγ to ^{99}Tc	γ: 0.14
Iodine-131 (^{131}I)	8.02 d	β^- to ^{131}Xe	β^-: 0.61 γ: 0.36
Caesium-134 (^{134}Cs)	2.06 y	β^- to ^{134}Ba	β^-: 0.66 γ: 0.6;0.8
Caesium-137 (^{137}Cs)	30.17 y	β^- to ^{137}Ba	β^-: 0.51 γ: 0.66
Cerium-144 (^{144}Ce)	284.8 d	β^- to ^{144}Pr	β^-: 0.3 γ: 0.13
Polonium-210 (^{210}Po)	138.38 d	α to ^{206}Pb	α: 5.3
Bismuth-210 (^{210}Bi)	5.01 d	β^- to ^{210}Po	β^-: 1.16
Lead-210 (^{210}Pb)	22.3 y	β^- to ^{210}Bi	β^-: 0.02; 0.06

Isotope	Half life*	Decay route(s) (branching fraction %)	Principal emission energies (MeV)
Polonium-214 (^{214}Po)	164 μs	α to ^{210}Pb	α: 7.7
Bismuth-214 (^{214}Bi)	19.9 m	β^- to ^{214}Po	β^-: 1.5; 3.3 γ: 0.61; 1.76
Lead-214 (^{214}Pb)	26.8 m	β^- to ^{214}Bi	β^-: 0.6; 0.7 γ: 0.3; 0.35
Polonium-218 (^{218}Po)	3.05 m	α to ^{214}Pb	α: 6.0
Radon-222 (^{222}Rn)	3.83 d	α to ^{218}Po	α: 5.5
Radium-226 (^{226}Ra)	1600 y	α to ^{222}Rn	α: 4.6; 4.8 γ: 0.19
Actinium-228 (^{228}Ac)	6.13 h	β^- to ^{228}Th	β^-: 1.2; 1.7 γ: 0.91; 0.97
Radium-228 (^{228}Ra)	5.75 y	β^- to ^{228}Ac	β^- : 0.04
Thorium-232 (^{232}Th)	1.41 x 10^{10} y	α to ^{228}Ra; sf	α: 4.0
Uranium-234 (^{234}U)	2.5 x 10^5 y	α to ^{230}Th; sf	α: 4.8
Protactinium-234 (^{234}Pa)	6.7 h	β^- to ^{234}U	β^- : 2.3
Thorium-234 (^{234}Th)	24.1 d	β^- to ^{234}Pa	β^- : 0.2
Uranium-235 (^{235}U)	7.0 x 10^8 y	α to ^{231}Th; sf	α: 4.4 γ: 0.19
Uranium-238 (^{238}U)	4.5 x 10^9 y	α to ^{234}Th; sf	α: 4.2
Plutonium-238 (^{238}Pu)	87.74 y	α to ^{234}U; sf	α: 5.5
Plutonium-239 (^{239}Pu)	2.4 x 10^4 y	α to ^{235}U; sf	α: 5.2
Plutonium-240 (^{240}Pu)	6563 y	α to ^{236}U; sf	α: 5.2
Americium-241 (^{241}Am)	432.2 y	α to ^{237}Np; sf	α: 5.5 γ: 0.06

*s: seconds; m: minutes; h: hours; d: days; y: years

Source: Adapted from Magill et al., 2006

Chapter 1 - Introduction

1.1. Thesis overview

In July 1955, eighteen Nobel Laureates attending the Lindau Nobel Laureates Meeting presented the following wording as part of the first Mainau Declaration:

> *We, the undersigned, are scientists of different countries, different creeds, different political persuasions. Outwardly, we are bound together only by the Nobel Prize, which we have been favored to receive. With pleasure we have devoted our lives to the service of science. It is, we believe, a path to a happier life for people. We see with horror that this very science is giving mankind the means to destroy itself. By total military use of weapons feasible today, the earth can be contaminated with radioactivity to such an extent that whole peoples can be annihilated. Neutrals may die thus as well as belligerents.* (Lindau, 1955)

The declaration came at a time when serious scientific alarm was being raised relating to nuclear fallout. The United States Castle Bravo test of the previous year, the first thermonuclear detonation, had led to widespread fallout in the Pacific and traces of the detonation being detected globally (List, 1955). At the time the primary apprehension related to direct external radiation effects that may result from fallout in a nuclear war. This was a prominent concern since the concept of a "salted bomb", seeded with cobalt to generate the highly radioactive cobalt-60 (^{60}Co), was being actively discussed (Arnold, 1950).

A consequence of the global fallout was that questions regarding the accumulation of radionuclides in agricultural systems and entry into the food supply began to be asked (Scott Russell, 1959). The knowledge of the internal exposure risks to radioactive substance preceded the atomic age with investigations into the health effects suffered by radium dial painters in the 1920s. Women working on the production lines for fluorescent dials

were being diagnosed with bone cancers, a diagnosis that was traced back to radiation damage from the internal exposure to radium (Fry, 1998).

However, with the discovery of the structure of deoxyribose nucleic acid (DNA) and how DNA structure related to function (Watson & Crick, 1953), the potential genetic effects from ionising radiation exposure began to be better understood. As a result the health implications of dietary exposure to radionuclides necessitated monitoring of food supplies where elevated radionuclides activities could occur. The United Nations Scientific Committee on Effects of Atomic Radiation (UNSCEAR), which was established in 1955, began collecting food supply activity concentrations for the fallout radionuclides caesium-137 (^{137}Cs) and strontium-90 (^{90}Sr), which it first reported the significance of in 1958 (UNSCEAR, 1958).

Whilst the era of atmospheric nuclear testing is now all but over, the health concern radionuclide contamination of the food chain still engenders is reflected in the modern day, most manifestly through the massive scale of food supply testing in Japan continuing on five years after the Fukushima-Daiichi civil nuclear accident of 2011. As of March 2016, approximately 1.36 million food samples had been analysed for caesium-134 (^{134}Cs) and ^{137}Cs contamination in order to monitor contamination resulting from the accidental release of radionuclides from this incident (MHLW, 2016). The accident is discussed in greater detail in Section 1.2.3.

Non-nuclear sources of contamination are also an emerging health concern. Radioactive elements, such as uranium and thorium, and their daughter radionuclides, are present in many minerals and soils and are naturally taken up into the food chain (UNSCEAR, 2000). The dietary burden from these naturally occurring radionuclides forms part of the normal background dose of radiation, along with a range of other sources such as radon (via inhalation) and exposure to cosmic rays. However,

through industrial utilisation and processing of these materials, concentration can occur. When these concentrated sources are then released into the environment, they may lead to an increase in the exposure to these natural radionuclides (IAEA, 2003). The dietary contribution and behaviour of the radionuclides in food chains from non-nuclear sources is not as well characterised as that from nuclear sources.

For New Zealand, where a large proportion of land use is for agriculture and primary production, the potential impacts of widespread radionuclide contamination could be significant to public health and the export economy. Some national monitoring has been undertaken since the 1950s (Hermanspahn, 2010;Matthews, 1993). This has largely focused on deposition of nuclear testing fallout using milk as a sentinel for uptake into the food chain. In comparison to research on other food contaminants, such as cadmium and lead which are extensively monitored in the New Zealand Total Diet Study (Vannoort & Thompson, 2009), the monitoring of radionuclides is severely limited in its ability to address current and future risks.

New Zealand has largely been protected from the largest atmospheric releases of anthropogenic radionuclides by its nuclear free status and its geographical isolation. However, radionuclides see widespread applications in modern society, including in medicine and engineering, from which release to the environment can occur (Fischer et al., 2009; IAEA, 2001). The potential for environmental releases from non-nuclear industries, such as mining and fertiliser use, also presents a risk of increasing the dietary exposure to radionuclides. Taking into account these factors, it is clear that geographic isolation alone is not enough to address all current and future food supply risks.

Identifying the full range of potential sources for radionuclide contamination of the New Zealand diet and the potential health

implications is necessary to begin to address food supply risks. This thesis sets out to quantify the current and future radiological risks to the New Zealand food supply.

1.2. Radionuclides and the sources of their environmental release

1.2.1. Radionuclides

Radioactive decay is the spontaneous process through which an unstable atomic nucleus releases energy. The resulting daughter nucleus is of a different element. A radioactive nuclide, commonly shortened to radionuclide, is any atom with an unstable atomic nucleus. Radioactive decay releases energy in the form of radiation. The emitted radiation is usually in the form of an α-particle (a nuclear fragment consisting of 2 protons and 2 neutrons) or a β-particle (a nuclear origin electron). The release of a γ-emission, a short wavelength, very high frequency photon, is not a primary decay process but can occur alongside α and β decay as excess energy is released from the daughter nucleus (Magill et al., 2006). Measurement and quantification of radionuclides is derived from the frequency and energy release by a radioactive decay, and for dose the energy absorbed by a tissue or individual. As a result radionuclide unit terminology differs considerably from that of stable chemistry Table 1.1. provides the definitions and units for the terminology used.

Table 1.1. Radiological units and terminology.

Term	Definition	Unit	Abbreviation
Absorbed dose	Radiation dose expressed in terms of absorbed energy per unit mass of tissue 1 Gy = 1 Joule/kg	Gray	Gy
Activity	Number of radioactive decays occurring in a given quantity within a set time period. 1 Bq = 1 decay per second	Becquerel	Bq
Branching fraction	Where a radionuclide can decay by different emission type the fractions of decays occurring along a certain route	%	-
Committed dose	The effective dose from internal exposure to a radionuclide, taking into account a time integral for duration of internal exposure	Sievert	Sv
Decay intensity	The percentage of decay emissions of a defined energy occurring in a radionuclide sample	%	-
Effective dose	The equivalent dose, with weighting factors placed for different tissue types if whole body exposure is non-uniform	Sievert	Sv
Emission energy	The energy of the ejected decay emission.	Electronvolt	eV
Equivalent dose	The absorbed dose, with weighting factors placed for different radiation types	Sievert	Sv
Fission yield	The yield of a fission product occurring from a nuclear fission	%	-
Half-life	The time constant for decay of half of the remaining atoms in a sample of a radionuclide	Time	$T_{1/2}$
Inventory	The calculated total amount of radionuclide activity in a certain area	Becquerel	Bq

Radionuclides are most commonly associated with nuclear fission, the splitting of atomic nuclei. The neutron-induced fission of a fissile isotope such as uranium-235 (^{235}U) or plutonium-239 (^{239}Pu), is the process by which energy is produced in a nuclear reaction (IAEA, 2007). Some radionuclides naturally undergo spontaneous fission, however in the environment this occurs at an extremely low rate. For example, the probability of spontaneous fission is 10^{-7} per decay for uranium-238 (^{238}U) and 10^{-9} for ^{235}U (Magill et al., 2006). The discovery of nuclear fission in the early 20th century led directly to the development of the nuclear power industry and nuclear weapons. As a consequence of nuclear fission, and its associated technology such as the activation of a nuclide through absorption of a free neutron, there is an ability to form a range of anthropogenic radionuclides that are naturally absent, or only present in trace quantities, in the environment. Examples of anthropogenic radionuclides include ^{60}Co, technetium-99 (^{99}Tc) and americium-241 (^{241}Am)

A range of radionuclides also occur naturally in the environment. These having been formed by natural stellar processes, such as supernova nucleosynthesis or cosmic-ray bombardment (UNSCEAR, 2000). Many abundant atomically heavy elements, such as uranium, thorium and bismuth, are inherently unstable and have no stable isotopes. Others, such as tellurium and rhenium, have a natural environmental occurrence of both unstable and stable isotopes (Magill et al., 2006).

1.2.2. Nuclear weapons

The 16th of July in 2015 represented the 70 year anniversary of the detonation of the first nuclear weapon, the 21 kiloton yield Trinity test undertaken in the Jornado del Muerto desert, New Mexico (US DOE, 2000). The date of the Trinity test is significant as this was the first case of widespread environmental distribution of anthropogenic radionuclides.

Following the test, anthropogenic radionuclides were reported to have been distributed over a large area of New Mexico (CDC, 2010). In the following 35 years an estimated further 543 atmospheric nuclear detonations occurred, all of which contributed additional unrestrained inputs of anthropogenic radionuclides to the global inventory (UNSCEAR, 2000). Notwithstanding any health implications, the magnitude and global coverage of the released pollutants represents one of the largest contamination events in the field of environmental chemistry. The long half-lives of many of the anthropogenic radionuclides from Trinity and subsequent tests will mean they remain detectable in the environment far into the future. For this reason the Trinity test has been suggested as a geochronological marker, a tracer that will remain detectable far into the future, for the boundary between the Holocene and Anthropocene historical eras (Zalasiewicz et al., 2015).

Close-in fallout from atmospheric tests has caused localised incidences of contamination in the food supply. Bikini Atoll, where the Castle Bravo testing noted in Section 1.1. occurred, is an example of where there have been serious health concerns from food contamination following nuclear tests in the region (Robison et al., 1997). The health concern was of a sufficiently significant magnitude that the Micronesian inhabitants, resettling after the end of testing, were again required to leave the atolls because of high doses of fission products. In dose assessments of the islands it was found that ^{137}Cs uptake from soil into food crops, in particular coconut trees, was a human health risk. It was estimated that a consumer of locally produced food would receive 15 times the acceptable annual dose limit (IAEA, 1997).

The widespread nature of the fallout from the atmospheric tests has meant that contamination is not restricted just to test site areas. In fact, low level contamination of global food supplies has occurred following

nuclear releases (UNSCEAR, 2000). Overall, global exposure through the diet peaked in 1962 at an annual committed dose of 0.047 mSv, at the time representing 43% of the dose to an individual, with the remainder mainly coming from external exposure. The contribution was largely from high activity of the short-lived Iodine-131 (^{131}I). As this decayed the predominant source of the ingestion dose from 1963 onwards became ^{137}Cs and ^{90}Sr. There was also a large contribution from the enhancement to the normal background levels of carbon-14 (^{14}C). The contribution of testing fallout to dietary ionising radiation dose in the 21st century following the cessation of testing is expected to be much lower. For example, the current average dose totalled for the years 2000 to 2099 is estimated at 0.14 mSv, predominantly from the circulation of enhanced ^{14}C activities in the food chain (UNSCEAR, 2000).

1.2.3. Nuclear power generation

Nuclear power plants (NPP) are currently operated in 30 countries, and a further 21 nations have previously operated or have plans to commission facilities (IAEA, 2015). At the end of 2014 there were 438 operational commercial reactors and a further 70 in construction worldwide. A further 150 reactors have been operational and are now permanently shut down. Nuclear power and its supporting fuel fabrication, reprocessing and storage/disposal presents a source of potential environmental release that requires significant management and long-term planning. Where releases have occurred in the past they have ranged in extent from small regulated local releases to large widespread accidental releases (IAEA, 2013; Vandenhove et al., 2013).

The Chernobyl accident in 1986 was one of the most well-known accidental nuclear releases and the joint highest on the International Nuclear Event Scale (INES) rating scheme (Kermisch & Labeau, 2013). The radioactive smoke from the reactor fire at Chernobyl led to contamination

of agricultural systems and marine food supplies throughout much of northern and central Europe (UNSCEAR, 2008). To manage the dietary doses, mitigation methods, such as depuration of sheep grazing in Cumbrian highlands (Beresford et al., 2007), have been, and continue to be, in force.

The most recent accidental release, for which the full environmental implications have yet to play out, is from the Fukushima-Daiichi NPP. In March 2011 a magnitude 9 earthquake and subsequent series of tsunamis hit the east coast of Japan and impacted on the Fukushima-Daiichi NPP (WHO, 2013). From the resulting damage to primary and backup systems, the reactor cooling systems in 3 of the 6 reactors failed leading to full or partial core meltdowns and hydrogen gas explosions. The environmental release of radionuclides from the Fukushima-Daiichi NPP accident can be characterised in two stages, the first being the atmospheric release occurring as a result of the reactor hydrogen explosions. This primarily contained volatile fission products such as ^{131}I and ^{137}Cs. A large proportion of the atmospheric fallout from these clouds was deposited offshore of the plant into the Northern Pacific ocean. The estimated ^{137}Cs release from Fukushima-Daiichi varies between 6-20 PBq (UNSCEAR, 2013). This is considerably lower than the 85 PBq released from Chernobyl. The second release consisted of the leakage of cooling water from overflow at the plant during the recovery operation. It was estimated that direct release into the ocean contributed 3-6 PBq of ^{137}Cs (UNSCEAR, 2013). Less volatile elements may have also been directly released. For example, a separate study estimated that 0.04-1 PBq ^{90}Sr may have also entered the marine environment (Povinec et al., 2012).

Aside from accidental releases many NPP sites may discharge some radionuclides to the environment as part of routine operations. Permitted liquid discharges from NPP sites are usually heavily regulated to limits

that will not result in impacts to human or environmental health. Investigations into the levels released by NPP sites indicate they are often far below the established regulatory limits (Vandehove et al., 2013). In some cases, however, permitted liquid discharges can lead to increased activity concentrations in local seafood as many of the radionuclides readily enter marine food chains. This is particularly true for discharges from nuclear fuel reprocessing plants, such as those at Sellafield, England and La Hague, France. The marine area around the nuclear reprocessing site at Sellafield is heavily monitored for the impact of discharges. In the analysis of the monitoring data there is good correlation in the decrease of regulated discharges of ^{60}Co and ^{99}Tc since 2003 and decreasing activity concentrations in tested winkles and lobsters (CEFAS, 2013).

A final consideration for radionuclide containment in the nuclear power process is the storage and disposal of used fuel and other radioactive waste. Long-term storage of used nuclear fuel or other radioactive wastes presents an ongoing challenge to limit sources of future contamination of ground-water or the marine environment. No repository currently exists for high level, long term storage, although a repository has recently been licensed for construction at Olkiluoto, Finland (Posiva, 2016). One factor influencing potential environmental impact is mobility, a property that determines the ability of a chemical to move through the environment. Thus the leaching of stored radionuclides, especially long-lived fission products may pose a threat to the environment, depending on their mobility. Consequently, risk assessment of potential storage sites is necessary as it may take millions of year for the stored radionuclide activity to decay to acceptable levels (Rodgers, 1983).

1.2.4. Other nuclear technologies

Nuclear technologies and radionuclides are used in many other fields outside of the nuclear industry. These include medical imaging, sterilisation, engineering and even within homes as components of smoke alarms (UNSCEAR, 2008). All of these uses present potential sources of environmental contamination, albeit often only at a local scale. (Fischer et al., 2009; Krawczyk et al., 2013; Nieves & Chen, 1995).

The United Kingdom monitors for radionuclides around many non-nuclear facilities, including sites generating radiopharmaceuticals (CEFAS, 2014). In this monitoring gaseous and liquid discharges from radiopharmaceutical manufacturing sites are reported to result in detectable levels of sulphur-32 and hydrogen-3/tritium (^{3}H), occurring in plant and fish sampled in the vicinity. Additionally a range of other radionuclides, including fluorine-18, sodium-22, ^{99}Tc, ^{131}I, neptunium-237 and curium-242, were reported to occur in liquid discharges from sites such as research establishments, hospitals and universities.

There are potentially serious implications associated with non-nuclear applications of radionuclides. This was demonstrated in the accidental release of ^{137}Cs in Goiânia, Brazil from a salvaged radiotherapy unit. The release of the ^{137}Cs lead to four fatalities and widespread contamination (IAEA, 1988). Fruit trees planted in this area have shown significant uptake of ^{137}Cs from the contaminated soil into fruit, which required mitigation actions many years after the accident occurred (Mosquera et al., 2006).

As a result of the risks associated with release of unsecured sources of radionuclides many countries have established radiation safety regulations. These can include guidelines for categorising a source, which for radionuclides is based on the activity, for tracking it and for ensuring it is secure (IAEA, 2009). Limits on the release of gaseous and liquid

radioactive effluents are also established based on criteria to ensure protection of human and environmental health (IAEA, 2000).

1.2.5. Naturally occurring radioactive materials

There is a natural abundance of the primordial radionuclides thorium-232 (^{232}Th), ^{235}U and ^{238}U in the Earth's crust (UNSCEAR, 2000). Daughter radionuclides produced from the initial decay of ^{235}U, ^{238}U and ^{232}Th also present an ongoing source of ionising radiation through the decay series which terminates at a stable lead isotope. Of importance to human exposure is the decay series of ^{238}U, historically termed the radium series (Figure 1.1.).

Primordial radionuclides without decay series, such as potassium-40 (^{40}K) and rubidium-87 (^{87}Rb), are also abundant in the environment. As well as shorter lived cosmogenic radionuclides, formed through interaction of high energy cosmic radiation with atmospheric particles, such as beryllium-7 (^{7}Be) and ^{14}C. Minerals containing appreciable concentrations of the primordial radionuclides and their decay series are collectively termed Naturally Occurring Radioactive Material (NORM).

Due to natural abundance in the environment in many cases NORM comprises a normal part of the diet. For example, the primordial radionuclide ^{40}K occurs at a natural ratio of 0.0117% to stable potassium so is ubiquitous in any food that contains potassium (Magill et al. 2006). A similar scenario exists for the cosmogenic ^{14}C (Magill et al. 2006). Furthermore, after formation in the atmosphere, the cosmogenic ^{7}Be undergoes wet deposition in precipitation, so activity concentrations of this radionuclide present in food will naturally fluctuate depending on timing of rainfall (Ioannidou & Papastefanou, 2006).

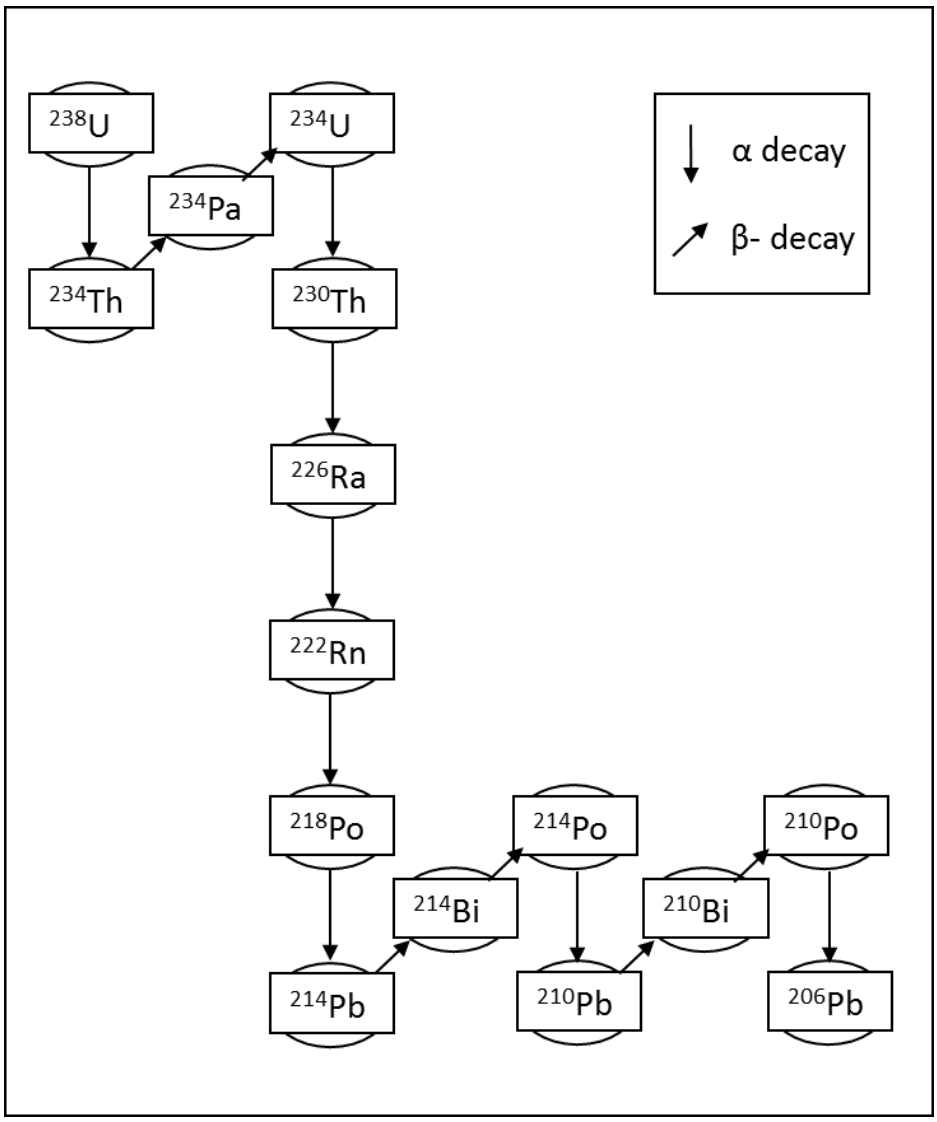


Figure 1.1. The ^{238}U decay series.

As certain minerals can have higher abundances of NORM, the extraction, processing and utilisation of deposits containing these minerals can lead to concentration of NORM. This technological enhancement of NORM (TeNORM) presents a risk for radionuclide entry into the environment from a number of industries which do not involve nuclear technology or nuclear fuel extraction (UNSCEAR, 2000; IAEA, 2006). The earliest radionuclide contamination of the environment would

have been a result of extracting NORM. Extraction of radium-226 (^{226}Ra) in the early 20th century led to sites in the United States that continue to require controls due to high contamination in the current day (USEPA, 2016). However regulatory focus and the development of strategies to mitigate TeNORM releases to the environment have only been prioritised over the last 20 years (Cowie et al, 2012; Government of Scotland, 2014; Health Canada, 2011).

TeNORM release can have significant implications in the food supply. TeNORM can lead to enhancement to the ionising radiation dose which in some cases can exceed that occurring from anthropogenic radionuclides. Whitehaven in the United Kingdom is an example where NORM uptake into seafood from a phosphate plant outflow far exceeded the dietary doses from nuclear origin radionuclide released from the nearby Sellafield NPP (CEFAS, 2014).

1.3. Environmental fate and the health implications of radionuclides

1.3.1. Environmental fate of radionuclides

Because of the wide variety of radionuclides that may enter the environment, the chemistry of these elements can differ significantly. For the nuclear origin radionuclides the different chemistries tend to be simplified into two groupings. The first grouping is of the highly mobile "volatile" elements, which includes the fission products ^{3}H, ^{131}I and ^{137}Cs. The second grouping is of the refractory elements which include the transuranics and the low volatility fission products such as zirconium-95 (^{95}Zr) and cerium-144 (^{144}Ce) (OECD NEA, 2002). In nuclear releases the former group present the widest contamination risk as they are readily transported in gaseous form and through environmental media. The refractory elements tend to present a localised risk around the release site. The dispersion is limited because release of the refractory elements tends to be in the form of airborne particles. These particles tend to travel

much shorter distances and see limited soil and water transport (UNSCEAR, 2000). Whilst the fallout tends to be localised there may be a more persistent risk as many of the refractory elements, in particular the transuranic elements, have very long half-lives.

The volatile radionuclides also have the greater uptake into plants and animals, as they accumulate with their stable isotopes (^{131}I with stable iodine and ^{3}H in tritiated water) or follow similar chemistry pathways (^{137}Cs with potassium; Prorok, 2016). Their potential gaseous nature also means they can contaminate plant surfaces following atmospheric deposition (IAEA, 2010). In animals there is generally a more rapid biological excretion of these elements as they do not bind significantly to ligands within tissues. The refractory elements show much more limited uptake into plants. For example, for ^{95}Zr there is practically no uptake (IAEA, 2010). In animals, while absorption of the refractory elements can be low, they can present a longer term risk of accumulation as they may persist in tissues and bone. The calculated biological half-life in humans for the transuranic elements plutonium, americium and neptunium, is 14 years in the liver, and in bone it is greater than the expected human lifespan (Taylor, 1989).

The environmental fates of the naturally-occurring radionuclides can also be highly varied. For the radium decay series radionuclides some elements like thorium and lead show low environmental mobility, whereas radium and to a lesser extent uranium are water soluble and can be transported throughout the environment (van der Loeff, 2001). The uptake into the food supply is also as varied. For example, ^{40}K is present in all foods containing natural potassium, whereas the uptake of the other natural radionuclides can differ significantly between plants, marine animals and terrestrial animals (IAEA, 2010).

1.3.2. Health implications of radionuclides

The ionising radiation that is emitted from the decay of a radionuclide presents health impacts to humans if absorbed into the body. The outcomes of acute and chronic radiation poisoning from large radiation doses are well documented, primarily as a result of epidemiological studies following the detonations of nuclear weaponry (UNSCEAR, 2000). The primary impact site of ionising radiation within the cell is the DNA. Damage to the DNA can result from direct ionisation of the nucleic acid molecules or through formation of reactive species due to excitations occurring on other cellular components (Kadhim et al., 2013).

Internal exposure to a radionuclide presents a risk as the source can be retained within the body leading to a prolonged exposure over time. As a result of the high kinetic energy of α and β- particles these represent the predominant hazard from internal exposure as these particles densely ionise the surrounding tissues (Riquier et al., 2013). Additionally, due to biochemical processes in the body, certain elements tend to accumulate in a particular organ or tissue type. Any radionuclides of these elements behave identically to the stable isotopes and thus can cause an increase in dose in certain tissue types. Strontium, for example, accumulates in bone, owing to its mimicry of calcium (Dahl et al., 2001). Iodine accumulates in the thyroid gland owing to the incorporation of this element into thyroid hormones. Consequently, the short lived fission product ^{131}I presents a concern as it is accumulated and consequently delivers concentrated β-radiation directly to the thyroid. This property of ^{131}I presents a serious immediate health risk in contamination scenarios following nuclear accidents. Concern over presence of ^{131}I in food stuffs in the immediate aftermath of the Fukushima-Daiichi accident led to a wide range of countermeasures in nearby prefectures, including restricting food sales and increasing the distribution of potassium iodide tablets (Murakami &

Oki, 2012). However, the propensity for ^{131}I to concentrate in the thyroid also allows it be used beneficially in nuclear radiotherapy of thyroid tumours (Lin & Chao, 2009).

A final noted consideration is that chemical toxicity is also a potential hazard for some of the radionuclide elements. In the case of uranium the long half-life of ^{238}U means that in isolation it is a greater chemical hazard than radiological, causing toxicity to the kidneys (EFSA, 2009).

1.4. Thesis objectives

1.4.1. Food security

The key overall goal of this thesis is to provide novel data that will contribute towards maintaining food security for New Zealand. The Food and Agricultural Organisation of the United Nations defines food security as the following:

> *A situation that exists when all people, at all times, have physical, social and economic access to sufficient, safe and nutritious food that meets their dietary needs and food preferences for an active and healthy life.* (FAO, IFAD & WFP, 2015)

A noted criterion to maintain food security is therefore that the food itself should be safe. Thus for any chemical or organism that can be detrimental to health, there is a strong obligation to minimise its presence in the diet.

Radionuclides as food contaminants, and the subsequent contribution to the human burden of ionising radiation, fall within this criterion. Establishing the acceptability of current exposures, and mitigating for any increases in future exposure, is important for maintaining food security, even for a developed nation such as New Zealand. The following objectives of this thesis set out timeframes of radiological risks to the New Zealand

food supply that will be considered in view of establishing current and future food security.

1.4.2. Gather data to support establishment of radionuclide baselines and a refinement of the New Zealand dietary radiation dose

No comprehensive survey of radionuclide activity concentrations in the New Zealand diet has previously been conducted. Monitoring of milk powder has historically been used as a sentinel for assessing uptake of nuclear fallout radionuclides from the soil (Figure 1.2; Matthews, 1993). Only ^{137}Cs is currently monitored for, as levels of the other major anthropogenic radionuclide of concern, ^{90}Sr, has dropped to trace levels (Hermanspahn, 2010).

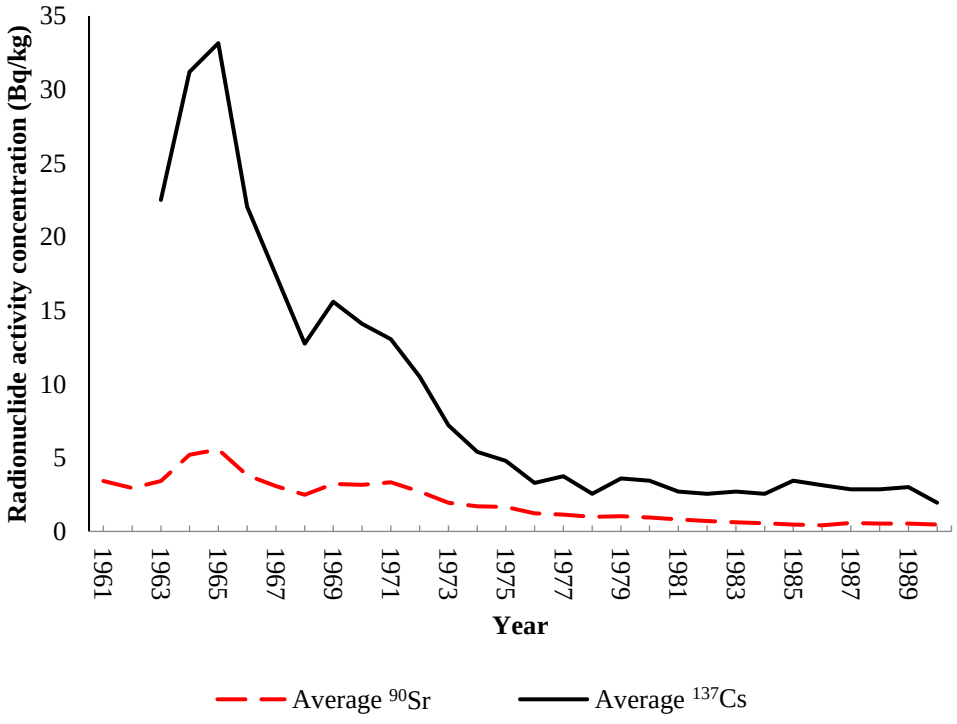


Figure 1.2. Trends of national mean New Zealand ^{137}Cs and ^{90}Sr activity concentrations in milk powder 1961-1990.

Source: Adapted from Mathews, 1993.

Nations with, or near to, nuclear power (e.g. Ireland or the United Kingdom), have comprehensive monitoring programmes that allow dietary radiation doses to be accurately calculated (CEFAS, 2014; RPII, 2014). The monitoring to date in New Zealand has not allowed this to occur. As a result, no baselines are available from which to estimate if sources of radionuclides are increasing in the diet. To address this lack of baseline it is necessary to establish the current activity concentrations of natural and anthropogenic radionuclides in a substantial proportion of the food supply. The derived activity concentrations will allow the corresponding population dietary burden to be calculated. Using the estimated dietary burden it is then possible to forecast for the impact of future risks to food security.

1.4.3. Gather data to quantify the potential short- and mid-term risks to enhancement of the dietary radiation dose

There are many sources of future risk to New Zealand food security from radionuclides. In the near-term a clear risk is the release of radionuclides from a nuclear accident or localised release. The Fukushima-Daiichi accident is the most recent large-scale release of anthropogenic radionuclides to the environment. The estimated initial ^{137}Cs release from Fukushima-Daiichi was 8.8 PBq in to the Pacific Ocean, with a further 5-8 PBq ^{137}Cs following from leakage of coolant following the initial input (UNSCEAR, 2013). The activity concentrations and the behaviour of ^{137}Cs in New Zealand's coastal environment are unknown, making it difficult to anticipate the contribution of a release of this scale to the dietary dose for seafood consumers. Additionally, the potential for localised releases of TeNORM into the marine environment from coastal industries and the transport of uranium ore or oil spills, can also present a radiological risk. To identify the significance that marine-borne

radionuclides may have on New Zealand seafood consumers, one aim of this thesis was to characterise the regional and species variation in ^{137}Cs and a naturally occurring radionuclide, polonium-210 (^{210}Po) in consumed seafood.

1.4.4. Quantify the factors influencing radiological risk, and forecast the future threat, to agriculture from phosphate fertilisers

Long-term radiological risks can be difficult to forecast. This is because the risks for nuclear origin radionuclides will be dependent on geopolitics and demands for nuclear energy. Focusing around a known scenario will allow a more definite estimate of risk. Therefore the future potential for radionuclides to enter the New Zealand food supply from non-nuclear sources is to be examined. The potential for industrial process to result in increased environmental activity of NORM has been gaining greater recognition overseas in the last 20 years. A number of countries (particularly heavily industrialised nations) and organisations, have proposed or established strategies to manage and mitigate the long-term risks from TeNORM releases to the environment (Cowie et al, 2012; Government of Scotland, 2014; Health Canada, 2011).

For New Zealand, a country with a focus on primary industries, NORM release has been less significant. Many of the major NORM producing industries, such as mining for mineral ores or fossil fuel generators, are absent or present in small volumes. However, the pastoral nature of New Zealand's agriculture and its requirement for suitable forage for intensive dairy and meat production does make New Zealand reliant on phosphate ores which can be a significant source of NORM. Determining the potential for NORM contamination of phosphate fertilisers as a long-term input to food producing land is an objective of the thesis. The purpose of this research is to establish if an upward trend in soil activity concentrations presents a long-term risk of increasing the dietary dose to NORM.

1.5. Thesis intent and structure

1.5.1. Thesis intent and focus

Internationally, a large body of work exists on radionuclide behaviour in the environment and the food supply. This thesis focusses on developing the New Zealand context to this research. New Zealand policies on nuclear energy and the geographic isolation of the nation make it relatively unique in terms of sources of anthropogenic radionuclide contamination. However, there is an absence of data on how non-nuclear sources of radionuclides may impact on the safety of the New Zealand food supply. There is also little published on future risk assessments to identify long-term radiological hazards to food security. Applying international ranges or means to a single country is often inaccurate as idiosyncrasies in agricultural system, dietary patterns and environmental transport can lead to scenarios where exposure may be over- or under-estimated. By specifically characterising the radiological risk and its associated factors for New Zealand its standing against international ranges can be established.

1.5.2. Academic papers

Material covered in Chapter Two has previously been published in Pearson et al., 2016a. Material covered in Chapter Four has previously been published in Pearson et al., 2016b.

1.5.3. Thesis structure

The thesis begins by examining the current food security risk of radionuclides to New Zealand before expanding on the future timescales, as established in Section 1.4. Chapter Two establishes the current dietary baselines for New Zealand, and Chapter Three uses this dataset to undertake detailed dietary exposure modelling. Chapter Four examines the current spatial and species variations in ^{137}Cs and ^{210}Po activity

concentrations for seafood and establishes if the potential for oceanic release of these radionuclides represents a short- to mid-term risk for food security. The next two chapters consider the long-term risks from NORM to New Zealand. Chapter Five explores the current ranges and fractionation properties of radium in New Zealand agricultural soils. The results from this research are then combined in Chapter Six with food crop uptake factors, fertiliser analysis and an increased soil contamination scenario to establish whether fertiliser-associated ^{226}Ra represents a credible long-term risk to New Zealand agriculture and food security. Chapter Seven collates all of the research outcomes to deliver a picture of current and future food security risks of radionuclide contamination for New Zealand. Additionally, recommendations are made in this chapter over potential interventions to mitigate for future risks as well as further research streams to address remaining questions.

Chapter 2 - Natural and anthropogenic radionuclide activity concentrations in the New Zealand diet

2.1. Introduction

Dietary surveys are an invaluable source of data for undertaking risk assessments for public health. Such surveys enable concentrations of contaminants and the impact of reduction programs to be identified over a number of years. In New Zealand, dietary surveys have been conducted for a number of decades. The most comprehensive of these is the New Zealand Total Diet Study which has been run seven times between 1974 and the most recent survey in 2009 (Vannoort & Thomson, 2009). An eighth study is currently being undertaken over the 2016 calendar year. These surveys have quantified estimates of health risk for the New Zealand population through exposures to a range of agricultural chemicals and contaminants in the diet.

Assessing radionuclide contamination in the diet is an important consideration in modern food safety. As outlined in Section 1.2. radionuclides can originate from a variety of sources and processes; either those occurring naturally, such as primordial or cosmogenic formation, or through human activities, such as release from nuclear weapons testing or accidents (UNSCEAR, 2000). Understanding the range of radionuclides in the diet and their respective activity concentrations is necessary to be able to quantify the risk of exposure. Characterising the current background activity of radionuclides in the diet makes it possible to better identify future contamination incidents and emerging long-term trends, and it enables possible mitigation before increasing levels of contamination become a significant health risk.

Chapter based on: Pearson, A.J., Gaw. S., Hermanspahn, N., Glover, C.N., 2016. Natural and anthropogenic radionuclide activity concentrations in the New Zealand diet. Journal of Environmental Radioactivity, 151:3, 601-608.

Radionuclide monitoring in New Zealand foods has focused on determining activity concentrations of ^{137}Cs, and up until 2000, ^{90}Sr in milk powders (Matthews, 1993). These data have been used to estimate the contribution of nuclear testing fallout radionuclides to the diet. Radionuclide activity concentrations in milk have declined following their peak at an average of 33 Bq/kg ^{137}Cs and 5.5 Bq/kg ^{90}Sr in 1965. The most recent study of activity concentrations in milk, in 2010, reported ^{137}Cs levels of 0.4-0.8 Bq/kg dry weight (dw) (Hermanspahn, 2010). However, no comprehensive survey of the radionuclide activity concentrations in other food types in the New Zealand diet has been conducted. It is unknown if milk remains an appropriate sentinel for radionuclide activity concentrations in the New Zealand diet.

Following the Fukushima-Daiichi Nuclear Power Plant accident in March 2011, global awareness has focused on the entry of imported foods with elevated anthropogenic radionuclide activity concentrations into the diet. New Zealand has previously implemented targeted monitoring; for example to determine ^{90}Sr and ^{137}Cs levels in fish from the North Pacific following the marine release from Fukushima-Daiichi (MPI, 2013). This study identified activity ranges for ^{134}Cs of 1.45-2.23 Bq/kg and for ^{137}Cs of 1.93-3.23 Bq/kg in mackerel from Japan, with no detections in tuna from Japan and in mackerel from other North Pacific nations. However results from imported food monitoring have had to be interpreted in isolation as the current ranges of radionuclides in the full New Zealand diet have not been characterised.

The objective of this chapter was to establish current activity concentrations for a number of natural and anthropogenic radionuclides across a range of food types available to New Zealand consumers. Targeted radionuclides were selected based on several criteria such as those previously identified or suspected to be present in the New Zealand

environment, and/or by reference to international regulatory limits established by Codex Alimentarius (CAC, 1995). Additionally, where no occurrence data were available for a radionuclide in New Zealand, prioritisation was made for inclusion based on the results from overseas dietary monitoring programmes such as the United States Food and Drug Administration total diet survey (US FDA, 2006) and the United Kingdom's Radioactivity in Food and the Environment reports (CEFAS, 2013). Interpretation of levels and comparison to results from other countries provides a useful benchmark to establish the current radiological status of the New Zealand diet. The other objective of this chapter was to assess the appropriateness of the current practice of using milk as a sentinel for radionuclide contamination of the New Zealand diet.

2.2. Materials and methods

2.2.1. Sample description

Forty foods were chosen for sampling (Table 2.1.). The majority of foods were domestically produced. Approximately 25% were seasonally imported and exclusively imported foods. Foods were selected based on prominence in the diet as determined from the New Zealand Total Diet Study (Vannoort and Thomson 2009). Other considerations such as potential for concentrating radionuclides and potential sentinels for specific types of agriculture or aquaculture were taken into account. For example, bottled water was selected over tap water due to the potential for higher activity concentrations of naturally occurring radionuclides in bore and artesian sources (EFSA, 2009). The foods tested were classified as fruits, vegetables, cereal grains, animal products, seafood, beverages and other foods. Wine was classified within fruit as it is the primary grape-derived product marketed in New Zealand.

Samples were obtained from a range of local supermarkets and wholesalers in the Christchurch and Wellington areas of New Zealand,

with the exception being wild pork samples, which were sourced from the North Canterbury area of New Zealand. Where possible, food samples were chosen from across important domestic production regions. For example, wine samples were selected so as to cover important viticulture regions of New Zealand, and shellfish and salmon were obtained from regions with aquaculture. Sampling was undertaken through the year of January 2013 to January 2014. Perishable samples were collected fresh during this period according to seasonal availability. Four samples of each food type were obtained. Pooled samples of fruit and vegetables consisted of 400-600 g of individual pieces. Meat and fish sample sizes were approximately 300 g and liquid samples were approximately 500-1000 ml. Cereal and miscellaneous foods were obtained pre-packed at various weights.

Samples were prepared by removing inedible components, for example peels, hulls, stones and shells. Non-liquid samples were then homogenised, prior to separation of portions for individual radiochemistry assays. Exceptions to this preparation were coffee which was freshly extracted, through an espresso machine, at a ratio of 1 g of beans to 10 ml water; and tea which for the beta and alpha emitter assays was prepared as the brewed drink at a ratio of 1 g of tea leaves to 100 ml water. All liquid samples, with the exception of olive oil, were acidified with 69% nitric acid to 0.1M to prevent sorption losses to container walls.

Table 2.1. Sampling regime for dietary survey of radionuclides sorted by food classes.

Fruits	Vegetables	Cereal Grains	Animal Products	Seafood	Beverages	Other
Apple (D)	Beans (D)	Breakfast cereal (M)	Beef steak (D)	Lemonfish (Rig shark) (D)	Beer (D)	Chocolate (M)
Banana (I)	Broccoli (D)	Flour (M)	Chicken breast (D)	Salmon (D)	Coffee (I)	Olive oil (M)
Kiwifruit (D)	Lettuce (D)	Oats, rolled (M)	Chicken egg (D)	Shellfish (D)	Tea (I)	Peanut (I)
Orange (M)	Mushrooms(D)	Pasta (I)	Honey (D)	Tuna (M)	Water, bottled (D)	Spice mix (I)
Peach (D)	Potato (D)	Rice (I)	Cow's milk (D)			
Strawberry (D)	Pumpkin (D)		Lamb's liver (D)			
Wine (D)	Sweetcorn (D)		Pork chop (D)			
	Tomato (D)		Wild pork (D)			

(D) Samples of New Zealand origin, (I) Samples of imported origin, (M) Samples of New Zealand and imported origin.

2.2.2. Gamma emitters

All food samples were screened for gamma emitting radionuclides using gamma spectroscopy. Samples were prepared in either a 400 ml cylindrical container or a 400-600 ml Marinelli beaker and analysed using CANBERRA high purity germanium (HPGe) semiconductor detectors. Samples were counted for a minimum of 172,000 seconds. All spectra were analysed using Genie 2000 software to derive activity levels for ^{40}K, ^{131}I, ^{134}Cs and ^{137}Cs. A proportion of the CANBERRA HPGe detectors were also calibrated to quantify activity levels of ^{60}Co and ^{241}Am and these radionuclides were reported in 82 samples.

2.2.3. Beta emitters

A pooled sample of all four replicates of each food type was analysed for the beta emitter ^{90}Sr. Samples were ashed at 500°C, prior to acid digestion with *aqua regia*, a mixture of Fischer Scientific analytical reagent grade nitric acid (69%) and hydrochloric acid (35%). Radiochemical separation was performed with an Eichrom Technologies Sr resin using the extraction chromatography principles in the ISO 18589-5:2009 standard method. The samples were then analysed by Liquid Scintillation using a QUANTULUS low-background liquid scintillation counter (LSC).

Stable strontium was used to gravimetrically estimate method recovery, by addition of 5 mg strontium in the form of strontium nitrate to each sample prior to acid digestion. Method precision was confirmed with a 95% recovery over five blank spike repeats.

2.2.4. Polonium-210

All samples were analysed for ^{210}Po, with the exception of a single tuna sample of which insufficient quantity was available to analyse. Perishable foods were dried at 80°C prior to digestion using *aqua regia*, with addition

of Labserve H_2O_2 (30%). Digestion of olive oil was preceded by saponification utilising saturated sodium hydroxide solution and 1 ml methanol to ensure even uptake of the yield tracer. Difficult matrices underwent a microwave digestion stage. The polonium isotopes were extracted from the digests by autodeposition onto silver disks. Plated disks were counted for 23 hours using Passivated Implanted Planar Silicon (PIPS) detectors in a CANBERRA alpha spectrometer (Appendix A, Figure A.1.). Polonium-209 (^{209}Po) was used as a yield tracer to estimate method recovery. Sample recovery, background counts and decay corrections were applied to back-calculate ^{210}Po activity on the date of sample collection. Sample preparation and analysis was undertaken within a month of sample collection to reduce the influence of ^{210}Po ingrowth resulting from lead-210 (^{210}Pb) decay.

Quality control of the ^{210}Po method was confirmed through the use of tracer blanks and a traceable ^{210}Pb solution containing ^{210}Po in secular equilibrium. A tenth of the samples were analysed in duplicate for quality control assessment. The mean percentage deviation between duplicate samples was 27.5%. This value is dominated by counting statistics.

2.2.5. Uranium-234, -235, -238 and plutonium-239+240

Uranium and plutonium isotopes were analysed in pooled samples comprised of the four samples of each of the food types. Samples were ashed and acid digested. Digests then underwent radiochemical separation following the protocol specified in Eichrom Technologies method ACW 16 VBS prior to undergoing counting for 23 hours using PIPS detectors in a CANBERRA alpha spectrometer (Appendix A, Figure A.2.). Uranium-232 and plutonium-242 were utilised as yield tracers to estimate method recovery.

2.2.6. Data analysis

Quality assurance of the radioanalytical methods was provided through the laboratory's participation in proficiency test exercises organised by the IAEA and the UK National Physical Laboratory (Dean et al. 2014; IAEA, 2013a). Background counts were obtained monthly for each analytical instrument. Additional steps included use of scintillant blanks in each batch run of the LSC and reagent and matrix spikes to validate methods for alpha spectrometry. Alpha spectrometry assays resulting in peak interference were repeated to obtain clearly defined peak counts.

Results for grains and spice mix are reported as Bq/kg dw. All other samples are reported as Bq/kg wet weight (ww) unless otherwise specified. Results for the radionuclides analysed by alpha spectrometry and ^{90}Sr are recovery corrected based on recovered yield tracer. Minimum Detectable Concentrations (MDCs) were calculated for each assay according to the method defined by Currie (1968). The MDC, also termed the detection limit, is the lower limit of a measurement at which there is a 95% level of confidence that a true positive detection will be recorded. This contrasts with the decision threshold, where the individual measurement meets statistical criteria to be above background at a level of confidence of 95%.

For most of the assays a high proportion of results below the MDC were determined. To provide estimates of the likely activity range all means were reported as upper-bound, where the calculated MDC was taken as the result for a non-detect and lower-bound, where zero activity was assumed for a non-detect. For gamma spectroscopy any indicative trace activities above the decision threshold but below the MDC have been reported.

2.3. Results and discussion

2.3.1. Anthropogenic gamma-emitting radionuclides

All 160 individual food samples were analysed through gamma spectroscopy. The resulting spectra were interpreted to derive activity concentrations and MDC for a range of gamma-emitting radionuclides. Of primary interest were the fission products ^{131}I, ^{134}Cs and ^{137}Cs which due to their volatility are environmental contaminants and human health risks in the short to medium term duration following a nuclear release. Activity concentrations for ^{60}Co and ^{241}Am were also reported due to their potential health significance if present in the diet, as evidenced by both having established Codex Alimentarius Guideline Limits in food (CAC, 1995). Data on the occurrence of either radionuclide in the New Zealand diet was also absent through which to indicate if contamination resulting from their use in non-nuclear applications was a concern.

The gamma emitting anthropogenic radionuclide ^{134}Cs was not detected in any of the 160 samples analysed (MDCs were in the range of 0.07-0.41 Bq/kg). As the Fukushima-Daiichi nuclear accident was the only large scale emission of ^{134}Cs in recent times, any detection of this isotope can be assumed to have come from Fukushima with almost certainty. For example, in Pacific bluefin tuna tested in the Eastern Pacific following the accident ^{134}Cs was detected with a mean activity of 4 Bq/kg dry weight (dw) (approximately 1 Bq/kg ww) (Madigan et al., 2012).

Activity of ^{137}Cs was quantified in five samples and indicative trace activity was reported in a further 19 samples covering all food classes but with highest frequency for seafood. The sampled marine fish included different fish stocks that are available to the New Zealand market with two Pacific Bluefin tuna of central Pacific origin, a single Southern Bluefin tuna of Southern Ocean origin and a locally caught Skipjack tuna. All the lemonfish were caught in New Zealand coastal waters. The occurrence of

^{137}Cs activity concentrations in all the marine fish samples from different stocks, coupled with the absence of ^{134}Cs activity concentrations, suggests the detected ^{137}Cs activity concentrations are not of Fukushima-Daiichi origin. Consistent with this assertion the ^{137}Cs results for tuna are comparable to activity concentrations reported prior to the Fukushima-Daiichi accident. For example, ^{137}Cs activity concentrations of 1.4 Bq/kg dw (approximately 0.35 Bq/kg ww) were reported in Pacific Bluefin tuna sampled in the Eastern Pacific in 2008 (Madigan et al., 2012). The reported levels of ^{137}Cs in fish for the current survey are also in similar ranges to those reported in surveys from other ocean bodies, including the Arabian Gulf and North Atlantic Ocean (Goddard et al., 2003; Carvalho et al., 2011).

Levels of ^{137}Cs reported in land-based agriculture produce were all at trace levels, falling below the calculated MDCs for the assay (Table 2.2.). These results indicate that no significant terrestrial radionuclide contamination is present. The pork and wild pork samples were all domestically raised or caught and as such the indicated activity concentrations of 0.05-0.16 Bq/kg likely represent the current residual level of ^{137}Cs in the New Zealand food chain from historical global fallout. Similar trace values for sweetcorn, potato and tomato, which were all domestically grown, also indicate a trace presence of ^{137}Cs in New Zealand soils. The presence of detectable ^{137}Cs in two milk samples is consistent with milk monitoring data for New Zealand collected over the last decade which indicates a trace presence from historical fallout (Hermanspahn, 2010).

Table 2.2. Detected wet weight activity concentrations and assay MDCs for ^{137}Cs in a survey of 160 foods from the New Zealand diet.

Food sample	Assay MDC (Bq/kg)	Reported activity concentration (Bq/kg)	Codex Alimentarius GL (Bq/kg)
Banana	<0.15	0.09	1000
Cereal	<0.26[a]	0.20[a]	1000
Lamb's liver	<0.13	0.07	1000
Lemonfish	<0.11	0.17	1000
Lemonfish	<0.19	0.16	1000
Lemonfish	<0.28	0.36	1000
Lemonfish	<0.11	0.13	1000
Milk	<0.15	0.08	1000
Milk	<0.13	0.07	1000
Peanut	<0.26	0.15	1000
Pork	<0.08	0.05	1000
Potato	<0.14	0.07	1000
Spice mix	<0.30[a]	0.18[a]	1000
Spice mix	<0.23[a]	0.12[a]	1000
Sweetcorn	<0.12	0.06	1000
Tea	<0.36[a]	0.27[a]	1000
Tea	<0.36[a]	0.21[a]	1000
Tomato	<0.15	0.09	1000
Tuna	<0.12	0.10	1000
Tuna	<0.38	0.44	1000
Tuna	<0.17	0.15	1000
Tuna	<0.16	0.27	1000
Wild pork	<0.20	0.16	1000
Wild pork	<0.12	0.06	1000

[a] Activity concentration expressed on a dry weight basis.

The detection of ^{137}Cs trace activity in two of the spice mixture samples and in two tea leaf samples, all of which were imported, are likely to be a factor of the degree of concentration of the ingredients in these foods and the potential for higher background ^{137}Cs in the Northern Hemisphere countries of origin. All of the detections reported for ^{137}Cs were, however, below the Codex Alimentarius guideline level of 1000 Bq/kg (CAC, 1995).

Trace activity of ^{131}I was reported in one shellfish sample. The validity of this result was confirmed with analysis of a follow-up sample from the same aquaculture site, which also reported trace ^{131}I activity. Due to the short half-life of this isotope (8.02 days) the presence of this radionuclide is unlikely to have originated from sources outside New Zealand. Other surveys from overseas have reported similar detections of ^{131}I in seafood (Goddard et al., 2003). A study in Australia confirmed that ^{131}I passes through wastewater treatment plants and is taken up by algae growing near the outfalls, with the majority of the ^{131}I present attributed to nuclear medicine patients (Veliscek Carolan et al., 2011). ^{131}I is used in New Zealand for radiotherapy (Beach, 2005), including in the region of the shellfish sampling site. As the shellfish sampling site was in close proximity to a wastewater discharge, medical origin is the probable source for the presence of trace levels of this radionuclide. The detected activity concentration of ^{131}I in the shellfish sample was less than 1% of the Codex Alimentarius guideline level of 100 Bq/kg (CAC, 1995)

^{60}Co and ^{241}Am were not detected in the 82 samples analysed. The MDC ranges for these two radionuclides were 0.10-0.49 Bq/kg and 0.05-0.27 Bq/kg respectively. Absence of any reported activity for ^{60}Co and ^{241}Am is consistent with other surveys, for example the US Food and Drug Administration Total diet survey (US FDA, 2005).

All the gamma spectra for the analysed food samples showed activity concentrations for ^{40}K. These ranged from bottled water at 1-6 Bq/L to tea leaves and spice mixes that had 300-1000 Bq/kg.

2.3.2. Beta emitters

Forty composite food samples were analysed for ^{90}Sr activity. ^{90}Sr was included in the survey as an important fission product for which historical monitoring in New Zealand indicated that terrestrial deposition occurred following global nuclear testing (Matthews, 1993). ^{90}Sr has an established Codex Alimentarius Guideline Limit in food of 100 Bq/kg (CAC, 1995).

Method recovery was calculated at 80-100% for all samples except the bottled water composite sample. For bottled water a 1.6 litre composite sample was used for analysis leading to lower recovery but greater method sensitivity. MDCs for ^{90}Sr ranged from 0.01-0.46 Bq/kg, and ^{90}Sr activity was absent in 39 of the assayed samples. ^{90}Sr activity was detected in only a single composite spice mix sample and the average of a duplicate assay on this sample gave an activity concentration of 0.46 Bq/kg.

Current New Zealand milk monitoring does not include ^{90}Sr as it had depleted to levels below the MDC at the start of the millennium (Hermanspahn, 2010). Its absence in all domestically produced samples from this survey reinforces this approach and indicates that fallout ^{90}Sr may have become bound in soils or leached below the root zone and is therefore unavailable for uptake into the food chain.

The single detect in the imported spice mix composite is likely to be a factor of the concentrated nature of the ingredients in this food, a consequence of drying. Additionally, due to the origin of all the spice mix samples from Northern Hemisphere countries it may reflect higher backgrounds of ^{90}Sr due to the greater global fallout in the Northern Hemisphere (UNSCEAR, 2000). For example, the presence of trace ^{137}Cs activity in two of the individual spice mix samples would support that the

presence of ^{90}Sr is as a fission product from residual nuclear fallout. Absence of ^{90}Sr in most food samples and the low level of ^{90}Sr detected in the spice mixture support the current practice of not monitoring for this radionuclide.

2.3.3. Polonium-210

^{210}Po was selected for analysis based on consideration of the high ionising radiation dose of each decay when ingested (ICRP, 2012) and a deficit of data on its magnitude in the New Zealand food chain. Additionally, reports from overseas have indicated elevation of ^{210}Po can occur in the food chain from anthropogenic sources (McCartney et al., 2000). A total of 159 samples were analysed for ^{210}Po. One tuna sample was unavailable for ^{210}Po assay as it had been ashed to improve gamma spectroscopy sensitivity. Method recovery varied between samples from 10-85%, dependent on the difficulty of acid digesting the sample. Average recovery across all foods analysed was 54%.

^{210}Po activity was absent in 56 of the analysed samples including all of the beer, broccoli, chicken, coffee, milk or pork samples. Calculated MDCs for bottled water were <0.0004 Bq/L, and for all other samples analysed ranged from <0.0045 to <0.1 Bq/kg dependent on sample volume and calculated recovery. ^{210}Po activity was determined in 103 of the analysed samples which encompassed a large variety of the foods (Table 2.3.). There was also considerable variation between the different food types, with activity concentrations ranging over five orders of magnitude. Most detected activity concentrations were, however, within the range of 0.005 to 0.05 Bq/kg. Of the samples sourced from terrestrial agriculture the highest ^{210}Po activity concentrations were determined in spice mix (1.3-5.6 Bq/kg). As with ^{90}Sr and ^{137}Cs these activity concentrations are likely to result from the high degree of concentration of the dried ingredients in these mixes. Levels in all other foods were below 1 Bq/kg.

Table 2.3. Upper-bound mean radionuclide activity concentrations from analysis of 159 samples for ^{210}Po and mean activity concentrations for 40 composite food samples for ^{234}U and ^{238}U.

Food	Radionuclide activity concentration (Bq/kg)			Food	Radionuclide activity concentration (Bq/kg)		
	^{238}U	^{234}U	^{210}Po		^{238}U	^{234}U	^{210}Po
Apple	0.005	<0.006	0.088	Mushrooms	0.004	<0.005	0.039
Banana	0.004	<0.004	0.018	Oats, rolled	0.010[a]	<0.005[a]	0.026[a]
Beans	0.005	0.005	0.012	Olive oil	0.002	<0.005	0.042
Beef steak	0.024	0.024	0.031	Orange	<0.002	<0.004	0.020
Beer	0.003	<0.008	<0.010	Pasta	0.068[a]	0.078[a]	0.049[a]
Breakfast cereal	0.011[a]	0.011[a]	0.080[a]	Peaches	<0.003	<0.004	0.091
Broccoli	0.007	0.005	0.013	Peanut	0.006	0.004	0.101
Chicken breast	0.043	0.051	<0.015	Pork chop	0.021	0.016	<0.016
Chocolate	0.014	0.014	0.093	Potato	<0.005	<0.008	0.011
Coffee[#]	0.015	<0.010	<0.009	Pumpkin	<0.003	<0.005	<0.009
Corn	0.003	<0.005	0.043	Rice	0.007[a]	<0.006[a]	0.076[a]
Drinking water	0.001	0.002	0.001	Salmon	0.013	0.012	0.068
Egg	0.006	<0.012	0.040	Shellfish	0.171	0.194	25.673
Flour	<0.002[a]	<0.005[a]	0.029[a]	Spice mix	0.250[a]	0.300[a]	2.486[a]
Honey	<0.065	<0.090	0.029	Strawberries	0.005	<0.006	0.019
Kiwifruit	0.004	<0.008	0.025	Tea[#]	<0.002	<0.007	0.028
Lamb's liver	0.067	0.087	0.643	Tomato	<0.003	<0.005	0.026
Lemonfish (Rig shark)	0.014	0.008	0.044	Tuna	0.040	0.041	3.659
Lettuce	0.013	0.018	0.018	Wild pork	0.016	0.018	0.182
Milk	0.001	0.006	<0.009	Wine	0.011	0.033	0.013

[a] Activity concentration expressed on a dry weight basis, [#] Analysed as prepared beverage.

Activity concentrations of ^{210}Po detected in New Zealand plant-derived foods were consistent with those reported overseas (CEFAS, 2013; Meli et al., 2014; Salahel Din, 2011). The ^{210}Po activity ranges for cereals, fruits and vegetables all were comparable to the reference values of 0.06, 0.04 and 0.1 Bq/kg stated by UNSCEAR (2000).

An interesting comparison between farm-raised pork and wild pork can be made. The farm-raised pork had no detectable activity concentrations of ^{210}Po whereas the wild pork had activity concentrations in the range of 0.063-0.43 Bq/kg. Similar differences have been found overseas in a comparative study of Italian wild and raised species (Meli et al., 2013). The authors hypothesised that higher levels in wild pork may be a result of increased deposition of ^{210}Po in forests and higher transfer through the diet. Both factors are also likely to be relevant for the difference in activity concentrations noted in the present study between the New Zealand wild and domestic pigs.

The highest activity concentrations of ^{210}Po were found in shellfish, with all four samples being in the range of 20.8-29.4 Bq/kg. These levels were likely due to accumulation of ^{210}Po- and ^{210}Pb-rich particulates by these filter feeders. Levels of this magnitude are common for bivalve molluscs and correspond to the ranges of levels detected in shellfish from other studies in Croatia, India, Slovenia, Taiwan and the United Kingdom (Lee & Wang, 2013; Rozmaric et al., 2012; Štrok & Smodiš, 2011; Sunith Shine et al., 2013; Young et al., 2002). Amongst the other aquatic species tested, activity concentrations of ^{210}Po varied. Tuna muscle had activity concentrations of 2.2-6.4 Bq/kg, and lemonfish and salmon showed activity concentrations of 0.03-0.1 Bq/kg in muscle tissue.

2.3.4. Uranium-234, -235, -238

As uranium is naturally present in New Zealand soils at levels between 1-3 mg/kg (equivalent to 12-37 Bq/kg ^{238}U; Schipper et al., 2011), detection

of activity concentrations in various commodities in the diet was expected. This study is presenting the first data on the uranium content of New Zealand food. Composite samples of each food-type, and individual shellfish samples, were analysed for alpha emissions corresponding to activity of the uranium isotopes uranium-234 (^{234}U), ^{235}U and ^{238}U. Of all analysed samples, 81% had detectable activity concentrations of ^{238}U and 54% had detectable activity concentrations of both ^{234}U and ^{238}U. Eight composite samples did not have any reported uranium isotope activity concentrations. These included peaches, tomato, oranges, pumpkin, potato, honey, flour and tea (Table 2.3.). Recoveries commonly ranged from 50-90% for uranium. High sugar content in samples, for example in honey and wine, decreased the method recovery, and in these samples recoveries of uranium ranged between 30-50%.

As ^{234}U is a daughter nuclide of ^{238}U, its activity in soils increases until equal to its parent; a state termed secular equilibrium (Rieppo, 1978). However, in water a phenomenon whereby variation of the activity ratio of ^{234}U: ^{238}U, towards ^{234}U, is often seen. This occurs as the initial decay of ^{238}U releases sufficient recoil to dislodge the daughter nuclide from the rocks in aquifers. The daughter nuclide and its further decay nuclides may become mobile in ground water due to this dislodgment and a change in the oxidation state of the daughter nuclide (Suksi et al., 2006). With use of ground water for irrigation the altered ratio is transferred to foods crops. Examples where ^{234}U: ^{238}U disequilibrium was evident in New Zealand-sourced foods for the current study include bottled water (2.1 ^{234}U/ ^{238}U), lettuce (1.4 ^{234}U/ ^{238}U), lambs liver (1.3 ^{234}U/ ^{238}U) and chicken breast (1.2 ^{234}U/ ^{238}U).

^{235}U was only detected in samples with the highest ^{238}U activity. Three samples of the 43 analysed had detectable activity concentrations of ^{235}U. These were spice mix, little-necked clams and lambs liver.

In New Zealand the range of activity concentrations for ^{238}U in fruit was <2.3-11 mBq/kg, and in meat was 16.2-67.1 mBq/kg; higher than the UN reference values of 3 and 2 mBq/kg respectively (UNSCEAR, 2000). As ^{238}U is naturally occurring this variation may be due to regional geological differences in uranium abundance. Another consideration is that many agricultural phosphate sources can contain significant uranium levels as a contaminant. Heavily fertilised agricultural soils could accumulate higher uranium levels. However, research on New Zealand soils, considering the potential for uranium contamination from phosphate applications, has indicated that annual accumulation is currently very low (Schipper et al., 2011). See Chapter Five for further discussion on the radionuclide activities in fertilisers.

The highest activity concentrations for the uranium isotopes, as for ^{210}Po, were reported in the shellfish samples, with one sample having 0.588 Bq/kg ^{234}U and 0.417 Bq/kg ^{238}U. The levels measured in shellfish are consistent with international data for uranium isotopes in seafood. For example, monitoring of mussels at sites around the coast of the United Kingdom identified levels of up to 0.841 Bq/kg, 0.028 Bq/kg and 0.758 Bq/kg for ^{234}U, ^{235}U and ^{238}U, respectively (Young et al., 2002).

Drinking water, in particular mineral water, can be a significant source for uranium dietary exposure (EFSA, 2009). The 1 mBq/L ^{238}U activity reported for the composite sample of New Zealand bottled waters is equal to the UN reference value for drinking water (UNSCEAR, 2000).

2.3.5. Plutonium-239+240

The plutonium isotopes ^{239}Pu and ^{240}Pu are a concern as dietary contaminants as they have high ingestion dose conversion coefficients (ICRP, 2012). A degree of atmospheric deposition from global fallout of ^{239}Pu and ^{240}Pu has been reported in New Zealand (Hancock et al., 2011), although transfer into the food chain has not been previously reported.

Composite samples of each food-type, and individual shellfish samples, were analysed for alpha emissions corresponding to activity of the plutonium isotopes ^{239}Pu and ^{240}Pu. Recoveries commonly ranged from 80-100% for plutonium, although as with the uranium assay high sugar content foods decreased the method recovery. In these samples plutonium recoveries were 55-70%. No $^{239+240}$Pu activity was detected in any of the food types analysed in this survey.

2.3.6. Activity concentration ranges

The developed upper-bound and lower-bound means and medians for radionuclides in the New Zealand diet are summarised in Table 2.4. Comparison to the Codex Alimentarius guideline levels for radionuclides indicates that dietary activity concentrations of anthropogenic radionuclides are orders of magnitude below those considered to be a risk to health (CAC, 1995).

The low frequency and magnitude of anthropogenic radionuclides detected in domestically produced foods is a likely reflection of several factors. First, historical nuclear fallout to the Southern Hemisphere has been lower than that to the Northern Hemisphere resulting in lower activity concentrations of anthropogenic radionuclides (UNSCEAR, 2000). Similarly, with no nuclear industry in New Zealand and very few nuclear power facilities in the Southern Hemisphere, contamination from local releases, either permitted or accidental, is not expected to have been significant for New Zealand.

However, while there is no nuclear power industry there is use of radionuclides in other fields, such as ^{131}I in medicine, ^{60}Co in irradiation facilities and ^{241}Am in home smoke detectors. By assigning expected ranges to all of the anthropogenic radionuclides it is possible to determine for future survey programs if additional sources or increased levels of contamination are present in the New Zealand food chain.

Table 2.4. Activity concentration ranges for radionuclides in a survey of 40 New Zealand food types, with comparison to relevant Codex Alimentarius Guideline Levels (CAC, 1995).

Radionuclide	Mean activity concentration (LB-UB) (Bq/kg)	Median activity concentration (LB-UB) (Bq/kg)	Codex Alimentarius Guideline level [a] (Bq/kg)
Potassium-40	96.56	73.63	n/a
Strontium-90	0.01-0.12	0-0.06	100
Iodine-131	0.001-0.13	0-0.12	
Cobalt-60	0-0.17	0-0.15	1000
Caesium-134	0-0.16	0-0.14	
Caesium-137	0.02-0.14	0-0.13	
Polonium-210	0.82-0.83	0.023-0.025	n/a
Uranium-234	0.043-0.047	0.0044-0.0077	n/a
Uranium-235	0.0008-0.007	0-0.0037	n/a / 100 [b]
Uranium-238	0.037-0.039	0.0064-0.0066	n/a
Plutonium-239+240	0-0.0052	0-0.0034	Infant food: 1; Other food: 10
Americium-241	0-0.12	0-0.11	

[a] *Guideline levels apply to the sum of activities from representative radionuclides, Guideline levels are not set for naturally occurring radionuclides;* [b] *^{235}U is only considered against the 100 Bq/kg guideline level when present from technologically enriched sources; levels at the natural environmental ratio are not considered.*

Of the naturally-occurring radionuclides ^{238}U and its decay series daughters can be influenced by anthropogenic factors and be concentrated in certain regions due to a range of industrial processes. These include mining, fertiliser manufacturing, fossil fuel extraction, power generation and drinking water filtration. The derived activity ranges provide a benchmark from which to analyse long-term trends of naturally occurring radionuclides in the food chain.

2.3.7. Sentinel foods

New Zealand monitoring for radionuclides in the diet has historically focused on milk, generally obtained in the powder form, as a sentinel. Activity concentrations have shown a consistent decrease from peak fallout from nuclear testing in the 1960's into the 2000's, with ^{90}Sr activity no longer being detectable. That no new contribution to activity has entered into New Zealand agriculture is consistent with the absence of significant fallout onto New Zealand since 1965 (Mathews, 1993; Tinker & Pilviö, 2000).

Milk analysed in the current study identified two samples with trace activity concentrations of ^{137}Cs, values consistent with the last New Zealand environmental monitoring report (MOH, 2013). Of the domestically sourced terrestrial agriculture samples only wild pork had a similar number of samples with measurable activity. No further anthropogenic radionuclides or ^{210}Po activity concentrations were detected in the milk samples, although a trace ^{238}U activity of 0.7 mBq/L was detected.

Milk has many benefits as a sentinel. First, it is consumed in significant volumes by the New Zealand population (Vannoort & Thompson, 2009) making any radionuclide present more relevant to the ingested dose. Second, it is produced in significant volumes throughout a large part of New Zealand and through a large part of the year, making obtaining monitoring samples simple. This is in contrast to many of the foods sampled in this survey that were only seasonally available. Finally, in comparison to many of the samples, milk is simple to process for the radiochemical analysis and good method recoveries were obtained for all of the assays. Milk in the form of powder also has a long shelf-life making retention of samples easier, and as a concentrate it gives lower MDCs than many fresh foods. The results of the current chapter suggest milk remains

a useful sentinel for ^{137}Cs, and it is therefore appropriate to maintain it as part of the New Zealand monitoring programme.

A number of imported foods in this survey had detectable activity concentrations of ^{137}Cs, including tea and spice mix. The spice mix sample also had a detected activity for ^{90}Sr. However the detected activity concentrations in the imported foods complies with the Codex Alimentarius guideline levels (CAC, 1995), indicating they do not represent a radiological risk. A specific sentinel for imported foods is not seen as necessary, however monitoring can be targeted to certain types of imported food where a risk of contamination exists. For example monitoring of tea from Japan for ^{137}Cs was undertaken in New Zealand following the Fukushima-Daiichi accident (MPI, 2013).

2.4. Conclusion

This survey of 160 food samples composing 40 food types common in the New Zealand diet has established activity ranges for different radionuclides of both natural and anthropogenic origin. Levels of the natural isotopes of uranium (^{234,235,238}U) and ^{210}Po showed the largest variation. Activity concentrations of uranium and ^{210}Po in shellfish were orders of magnitude greater than other food types. ^{238}U and ^{210}Po were also the most frequently detected radionuclides across the foods sampled. In contrast, detection of anthropogenic radionuclides in the New Zealand diet is infrequent and of low activity, with the absence of many anthropogenic radionuclides an indicator of the isolation of New Zealand from nuclear activities. The activity concentrations of radionuclides in the New Zealand food supply are equal to, or less than, those of other countries. Finally milk, in the form of powder, remains a suitable sentinel for anthropogenic radionuclides in New Zealand terrestrial agriculture.

Chapter 3 - Deterministic and semi-probabilistic modelling of the committed dose from radionuclides and the chemical burden from uranium in the New Zealand diet

3.1. Introduction

No detailed dietary radionuclide surveys have previously been completed in New Zealand, as a result, to date, no refined estimate of the contribution from the diet has been possible. In Chapter Two the activity concentrations of thirteen radionuclides were established across a range of New Zealand foods. Using these values it is possible to undertake dietary modelling to refine the dietary dose estimate for the New Zealand population.

Due to its long half-life ^{238}U can be present in the environment in significant concentrations. In its soluble forms it is of moderate chemical toxicity and has been raised as a concern in some regions due to high levels being present in drinking waters (EFSA, 2009). As ^{238}U activity concentrations were determined in New Zealand foods as part of the dietary survey in Chapter Two it is also possible to undertake an exposure assessment for uranium as a chemical toxicant.

Various forms of ionising radiation can affect biological tissue in different ways dependent on the linear energy transfer, the energy an ionising particle transfers to a material whilst traversing a distance. For example, the ionisation potential of an alpha particle makes it more damaging than a gamma or x-ray (IARC, 2009). Due to this, the absorbed dose to biological systems from ionising radiation (the Gray (Gy)) is adjusted with a quality factor to calculate the biologically committed dose (the Sievert (Sv); ICRP, 2007). The health impacts of ionising radiation have been divided into deterministic (or tissue-reaction) and stochastic effects.

Deterministic effects are those that generally occur after acute exposure to high doses of radiation. The high degree of ionisation is sufficient to cause rapid tissue damage and usually results in a condition termed acute radiation syndrome (UNSCEAR, 2013). Acute radiation syndrome generally occurs after doses in excess of 1 Gy (López & Martín, 2011). The large dose of radiation causes significant cell death. This cell death is most marked in the bone marrow and the small intestine due to their high rates of cell turn-over. The damage manifests as vomiting and lymphocyte depletion. Other effects such as skin burns, hair loss and hypothyroidism combine to make diagnosis of the deterministic effects of irradiation straightforward to trained medical professionals (UNSCEAR, 2013). At doses of above 10 Gy damage to the neurovascular system is usually enough to prove fatal rapidly after exposure. Whilst contamination of the food supplies to levels that could cause deterministic health effects is unlikely on a population basis there are examples where the diet has been a route of acute exposure to an individual or groups. Accidental consumption of ^{137}Cs was implicated in some of the Goiânia accident fatalities reported on in Section 1.2.4. (IAEA, 1988), and the deliberate fatal poisoning of Alexander Litvinenko with ^{210}Po occurred from internal exposure (Maguire et al. 2010).

Stochastic effects are those where the level of dose is not immediately lethal to cells, yet the resulting changes to the cell increase the probability of a long term adverse health outcome. An example of a stochastic effect is radiation-induced carcinogenesis (UNSCEAR, 2013). Generally, this is caused by the generation of chromosomal aberrations resulting from DNA damage (Tucker, 2008). The latency period between exposure and manifestation of a disease can be many years. As a result stochastic effects are not always clearly traceable to exposure to ionising radiation. However, on a population basis increased disease prevalence can be traced

to an exposure and this generally increases as the dose increases (UNSCEAR, 2013).

No dose threshold has been established for the stochastic effects of ionising radiation, which may present a risk at low doses. Because of the potential latency of stochastic effects, risks from exposure to radiation doses are considered on a lifetime basis. The lowest annual dose clearly linked with an increase in cancer is 100 mSv (US NAS, 2006). For the purposes of protection of public health, a reference dose level 100-fold lower (i.e. 1 mSv) has been adopted for exposure to non-natural sources (ICRP, 2007).

Minimising exposure of workers and the general public to ionising radiation underpins the safeguards placed on handling and storing radioactive materials, and ensures nuclear accidents are a global concern. However, on a daily basis general populations are exposed to various forms of radiation, ranging from cosmic rays, to decay of naturally occurring radionuclides in the soil and diet, in addition to anthropogenic sources (UNSCEAR, 2008). These latter forms of exposure may be either intentional, such as in medical imaging, or unintentional through the presence of nuclear contaminants in the environment (UNSCEAR, 2000). Understanding the sources and intensities of these exposures is important to determine long-term risk to the population.

Many radionuclides are readily taken up by food crops and can accumulate in certain edible species. The significance of these radionuclides activity concentrations to human health requires the calculation of the resulting dose. Due to the differing decay properties of radionuclides, and their kinetics in the body, their contribution to committed dose can vary (ICRP, 2012). Furthermore, consumption patterns of different food sources across a population vary widely in terms of diet composition and quantities consumed. To be able to account for

this information dietary modelling of the exposure is required to identify which foods and radionuclides are contributing to the dose. This approach enables higher exposure sub-populations to be identified. By identifying if dietary radiation is a concern risk management actions can be undertaken in response to any contamination of the diet that may be occurring.

Dietary radionuclide surveys are regularly conducted overseas, and the scope of these can vary from focusing on certain types of radionuclides or selective food types. Total diet survey work has been undertaken by a few countries to establish estimates of ingestion dose of ionising radiation, with calculated doses ranging from 267 μSv/yr in Ireland to 800 μSv/yr reported in Japan (RPII, 2014; Ota et al., 2009). Differentiation of the dose contribution from natural and anthropogenic radionuclide has been undertaken in the United Kingdom with the former being estimated at 250-323 μSv/yr and the later <5-61 μSv/yr (CEFAS, 2014; Watson et al., 2005). The United Nations Scientific Committee on the Effects of Atomic Radiation (UNSCEAR) has calculated global averages of the contributions of various sources of natural radiation to the total dose, and based on this, the average ingested dose is 290 μSv/yr with a range between 200 and 1000 μSv /yr (UNSCEAR, 2008).

Estimates for total ionising radiation exposure in New Zealand have previously been published by the National Centre for Radiation Science (ESR, 2011). The total annual dose from all sources is estimated at 2.31 mSv per person, from which natural radiation sources account for 78% of the estimated dose and medical sources 21%.

The objective of this chapter was to establish the current dietary burden to the New Zealand population from radionuclide and uranium exposure in the food chain. The annual committed dietary doses of ionising radiation for different age and gender groups of the New Zealand

population was calculated. From this significant contributing food groups and radionuclides were identified.

3.2. Methodology

3.2.1. Activity concentrations

Activity concentrations for thirteen radionuclides across forty foods in the New Zealand diet were established in Chapter Two. The analysed radionuclides were ^{40}K, ^{60}Co, ^{90}Sr, ^{131}I, ^{134}Cs, ^{137}Cs, ^{210}Po, ^{234}U, ^{235}U, ^{238}U, $^{239+240}$Pu and ^{241}Am. A number of radionuclides did not have activity detected above the minimum detectable concentration (MDC), termed left-censored results. To allow a full exposure model to be undertaken, representative activity values have had to be assigned to the left censored results. To address the potential range from absence of radionuclide activity in these foods to a results that falls just below the MDC two values have been used in the model to allow a probable dose range to be derived. Firstly the upper-bound mean activity (UB), whereby activity concentrations are assigned to the value of the MDC. Secondly the lower-bound mean activity (LB), where activity concentrations are assigned to zero.

Conversion of the activity concentration (Bq/kg) to the committed dose (Sv) differs depending on the radionuclide and the age of the consumer. Based on published studies, the International Commission on Radiological Protection (ICRP) has collated the conversion factors for a wide range of radionuclides (ICRP, 2012). To determine the effective dose from the activity concentrations of the thirteen radionuclides analysed for the different age groups, ICRP age-dependent dose coefficients were used (Table 3.1.).

3.2.2. Deterministic dietary exposure

A deterministic dietary exposure model was constructed in Microsoft Excel 2013 to provide point estimates of the annual committed dose for different age and gender groupings in the New Zealand population. The model assigned exposure based on the mean estimated consumption for each age group in the population against a mean activity concentration for each food (Equation 3.1.).

Equation 3.1. Deterministic dietary exposure calculation used to establish annual committed dose from ingested radionuclides.

$$D = 365.25 \times (Q \times \Sigma(C \times I))$$

Where D is the Annual Committed Dose for the radionuclide of interest (μSv/yr), Q is the dose coefficient for the radionuclide (Table 3.1.), C the mean activity concentration for the radionuclide in a food (Bq/kg) and I its average daily intake (g/day). A factor of 365.25 day/year is included to convert the daily dose to an annual dose.

The mean daily consumption values from the two-week simulated diet in the 2009 New Zealand Total Diet Study (09NZTDS) were used as the basis for assigning consumption quantities to each food commodity (Vannoort & Thompson, 2009). In order to assign activity concentrations to the majority of the simulated diet a process of mapping the intake values for foods in the 09NZTDS simulated diet to the food types sampled in Chapter Two was undertaken. Foods were mapped where the analysed food was sufficiently similar in description or could be seen as being representative of the food or crop type in the simulated diet. Using the example of tomato, this was directly representative of the raw and processed tomato commodities reported in the 09NZTDS. Additionally as a closely related fruiting vegetables tomato was also considered representative of capsicum. The calculated tomato intake value for the

dietary model was therefore mapped out as the sum of intakes of raw and processed tomato commodities and raw capsicum from the 09NZTDS simulated diet. Based on the mapped foods, consumption values for each commodity were compiled to represent an average daily intake for each age/gender grouping (Table 3.2.).

Table 3.1. ICRP age-dependant dose coefficients for age groups and radionuclides of interest for dietary exposure assessment (ICRP, 2012).

	Age group dose coefficients (1 Bq = x µSv)			
Radionuclide	**Adult 25 yrs+**	**Teen 15 yrs**	**Child 5 yrs**	**Toddler 1 yr**
^{40}K	6.2×10^{-3}	7.6×10^{-3}	0.021	0.042
^{60}Co	3.4×10^{-3}	7.9×10^{-3}	0.017	0.027
^{90}Sr	0.028	0.080	0.047	0.073
^{131}I	0.022	0.034	0.10	0.18
^{134}Cs	0.019	0.019	0.013	0.016
^{137}Cs	0.013	0.013	9.6×10^{-3}	0.012
^{210}Po	1.2	1.6	4.4	8.8
^{234}U	0.049	0.074	0.088	0.13
^{235}U	0.047	0.070	0.085	0.13
^{238}U	0.045	0.067	0.080	0.12
$^{239+240}$Pu	0.25	0.24	0.33	0.42
^{241}Am	0.20	0.20	0.27	0.37

Table 3.2. Mean consumption values for age/gender cohorts for the 40 food commodities assessed for radionuclide exposure.

Food	Mean Consumption (g/day)*						Food	Mean Consumption (g/day)*					
	AM	AF	TB	TG	C	T		AM	AF	TB	TG	C	T
Apple	87	79	82	89	90	57	Mushrooms	4	6	4	3	1	1
Banana	34	34	26	19	30	35	Oats, rolled	24	11	5	6	5	9
Beans	35	27	25	19	15	12	Olive oil	26	16	15	11	9	6
Beef steak	122	67	108	81	54	39	Orange	44	47	35	57	50	39
Beer	386	32	0	0	0	0	Pasta	68	46	63	63	46	33
Broccoli	10	14	9	6	6	5	Peaches	25	28	11	12	17	10
Cereal	22	16	28	18	21	22	Peanut	5	2	6	4	5	1
Chicken breast	59	48	65	46	34	12	Pork chop	28	17	24	14	9	8
Chocolate	42	41	77	66	64	22	Potato	157	92	145	130	89	41
Coffee	436	425	7	11	0	0	Pumpkin	16	13	5	6	6	8
Corn	8	6	5	4	6	2	Rice	32	29	26	14	16	4
Drinking water	218	296	347	348	371	251	Salmon	20	13	12	5	3	2
Egg	22	18	16	14	11	8	Shellfish	7	3	1	1	0	0
Flour	166	128	204	163	147	69	Spice mix	0.5	0.5	0.5	0.5	0.5	0.5
Honey	5	3	3	2	2	1	Strawberries	9	8	4	5	3	2
Kiwifruit	4	6	1	3	6	4	Tea	421	471	18	18	14	0
Lamb's liver	2	2	0	0	0	0	Tomato	56	47	36	33	14	13
Lemonfish	10	7	8	6	9	6	Tuna	5	4	3	3	1	1
Lettuce	16	14	14	9	2	1	Wild pork	13	8	8	6	3	1
Milk	362	291	279	222	250	402	Wine	43	54	1	2	3	1

*AM: Adult Male (≤25 yrs); AF: Adult Female (≤25 yrs); TB: Teenage Boy (15 yrs); TG: Teenage Girl (15 yrs); C: Child (5 yrs); T: Toddler (1 yr)

This “commodity mapping” exercise was not able to account for all components of the full simulated diet with such foods as carbonated beverages, soy milk and yeast extract not having an appropriate proxy in the radionuclide activity survey. To estimate a full dietary burden for each age/gender cohort a correction factor was included based on the ratio of the mapped diet for each age group against the total simulated energy intake in the 09NZTDS (Table 3.3.). This is based on an assumption that the mean activity concentrations of the thirteen radionuclide across the 40 food tested reflect those in the other food types in the simulated diet. The calculated factor was applied to the final exposure value to determine the estimated dietary exposure. Exposures for each age and gender group were then calculated using the UB and LB mean activities for each radionuclide recorded in Chapter Two and converted into μSv by the use of the applicable dose coefficient (Table 3.1.). The calculated committed dose represents a single day’s exposure; the total was multiplied by 365.25 day/year to obtain an annual committed dose for each radionuclide.

Table 3.3. Mapped diet values for age/gender cohorts and correction factors to account for full dietary energy intakes.

Food	Consumption (g/day)*					
	AM	**AF**	**TB**	**TG**	**C**	**T**
Mapped diet total	3049.5	2469.5	1726.5	1519.5	1412.5	1128.5
09 NZTDS simulated total	3474	2792	2051	1797	1633	1275
Conversion factor	1.139	1.131	1.188	1.183	1.156	1.130

*AM: Adult Male (≥25 yrs); AF: Adult Female (≥25 yrs); TB: Teenage Boy (15 yrs); TG: Teenage Girl (15 yrs); C: Child (5 yrs); T: Toddler (1 yr).

A reference dose for existing exposure situations has not been legislated in New Zealand. In the absence of a formal reference dose level the lower range of the ICRP reference levels (2007), 1 mSv/yr, has been

adopted in this work as a suitable health based guidance value to characterise the risk of dietary ionising radiation exposure.

3.2.3. Semi-probabilistic modelling

A semi-probabilistic method relies on the same concept as the deterministic model; however it uses a full dataset from a nutrition survey so as to provide a more reliable measure of consumption patterns across a population. By modelling the likely exposure for each of the several thousand respondents in a nutrition survey a more population-realistic estimate of exposure can be attained relative to that calculated from an average consumption value. It also gives a greater ability to determine consumption patterns for individuals that may lead to higher daily exposures, and how prevalent these are in a population.

The proprietary Food Standards Australia New Zealand HARVEST dietary modelling software was used to construct two semi-probabilistic models. The first model for New Zealand adults used consumption values obtained from the 2008 New Zealand Adult Nutrition Survey (08ANS), and a second, for children, used the 2002 New Zealand Children's Nutrition Survey (02CNS) (MOH, 2003; University of Otago & MOH, 2011). The model calculates all intakes in processed foods back to raw commodity or semi-processed commodity intake values. For example tomato on a pizza or in tomato sauce is converted back to the equivalent intake of raw tomatoes.

To ensure the widest coverage of New Zealand dietary patterns, all foods were assigned against the relevant category under the Codex Alimentarius Classification of Foods and Feeds (CAC, 1993). From here the foods tested from Section 2.2.1 were mapped to the most appropriate overarching crop or species grouping. For example, activity concentration values in apples (FP0226) were assigned to all dietary entries containing

consumption of raw or processed pome fruits (FP); similarly salmon (WD0121) to all diadromous fish (WD). On this basis the tested foods act as proxies for radionuclide activity concentrations across similarly grouped crops and edible tissues throughout the diet. A small number of semi-processed and processed foods were analysed in the dietary survey. In the instances where a semi-processed food grouping was unavailable, the food was mapped against its primary constituent crop or semi-processed commodity. For example, breakfast cereal was mapped to unprocessed cereal bran (CM0081). Finally, certain food groupings contained two or three foods that were tested. For example, the classification for other fruiting vegetables (VO) contained mushrooms, sweetcorn and tomatoes, while marine fish (WM) contained tuna and lemonfish. In such situations the foods with the highest activity was mapped to the crop grouping with other values being assigned only to the individual food type analysed.

Exposures across the survey respondents were calculated using the UB and LB mean activities for each radionuclide reported in Chapter Two and converted into μSv by the use of the applicable dose coefficient for either an adult or 5 year old child. The only exception was ^{40}K as its internal dose generally remains constant if the natural isotopic ratio remains unchanged. Mean and 97.5th percentile ingested doses across both the 08ANS and 02CNS survey populations were calculated.

3.2.4. Uranium chemical exposure

Activity concentrations for ^{234}U, ^{235}U and ^{238}U across forty foods in the New Zealand diet were established in Chapter Two. A chemical concentration of uranium was calculated through conversion of the Bq/kg ^{238}U to mg/kg, using a conversion factor of 1 Bq/kg ^{238}U= 0.081mg/kg ^{238}U.

The deterministic dietary exposure assessment for uranium used the mapped diet as derived in Table 3.2. As with the radiological modelling a

correction factor was applied to the diet to account for the full intake for each age group. Exposures were then calculated in Microsoft Excel 2013 for each age group using a standard dietary exposure calculation and age/gender body weights from the 09NZTDS (Equation 2.2.; Vannoort & Thompson, 2009).

Equation 2.2. Chemical dietary burden calculation for uranium

$$E = \Sigma(C \times I)$$

Where E = Dietary exposure in mg/kg bw/day, C = Concentration in a surveyed food in mg/kg and I is the intake of that food in mg/kg bw/day. All dietary exposure values for uranium are expressed as percentages of the World Health Organization Tolerable Daily Intake (WHO TDI) for soluble uranium (0.0006 mg/kg bw/day) (WHO, 1998).

3.3. Results and discussion

3.3.1. Deterministic dietary dose assessment

Deterministic exposure calculations were run for all UB and LB mean activity concentrations of each of the food types collected in Chapter Two. The deterministic model established the estimated upper and lower bound annual committed dose for each of the radionuclides in the diet (Table 3.4.).

Table 3.4. Deterministic exposure estimate of the annual committed dose for different age/gender groupings through radionuclides in the New Zealand diet. Using upper-bound(UB)and lower-bound (LB) mean activities.

Radionuclide	Mean dietary radionuclide exposure (LB-UB) (μSv/yr)					
	Adult male	Adult female	Teenage boy	Teenage girl	Child	Toddler
^{60}Co	0-0.54	0-0.50	0-0.63	0-0.54	0-1.03	0-0.97
^{90}Sr	0.003-2.67	0.003-1.98	0.01-5.94	0.01-4.89	0.005-2.51	0.01-2.38
^{131}I	0.003-3.90	0.001-3.31	0.001-3.09	0.001-2.66	0-7.06	0-10.42
^{134}Cs	0-3.96	0-3.40	0-1.99	0-1.72	0-1.06	0-1.05
^{137}Cs	0.40-2.44	0.40-2.08	0.12-1.20	0.10-1.04	0.07-0.69	0.10-0.67
$^{239+240}$Pu	0-1.22	0-0.95	0-0.51	0-0.44	0-0.51	0-0.50
^{241}Am (revised MDC)	0-21.36 (0-0.98)	0-18.32 (0-0.76)	0-11.54 (0-0.43)	0-10.15 (0-0.37)	0-12.07 (0-0.42)	0-9.94 (0-0.44)
Sub-total Anthropogenic[1]	0.41-15.71	0.40-12.98	0.13-13.79	0.11-11.66	0.08-13.28	0.11-16.43
^{210}Po	124.23-134.33	68.09-74.81	50.28-58.37	47.08-53.66	61.57-76.85	76.89-102.24
^{234}U	0.40-0.71	0.30-0.53	0.52-0.66	0.44-0.56	0.40-0.52	0.44-0.54
^{235}U	0.0002-0.27	0.0002-0.21	0.0001-0.15	0.0001-0.13	0.0002-0.13	0.0002-0.15
^{238}U	0.45-0.50	0.34-0.38	0.42-0.46	0.35-0.39	0.31-0.34	0.30-0.32
Sub-total NORM[2]	125.53-135.81	68.73-75.93	51.22-59.64	47.87-54.74	62.28-77.84	77.63-103.25
Total[1]	125.94-151.52	69.13-88.91	51.35-73.43	47.98-66.40	62.36-91.12	77.74-119.68

[1] Calculated using revised UB dose from ^{241}Am.

[2] Excludes the fixed dietary dose contribution of 165 μSv/yr for adults and 185 μSv/yr for children resulting from ^{40}K (UNSCEAR, 1993)

Activities of anthropogenic radionuclides in all of the foods analysed were low to undetectable. Consequently all of the exposures for the anthropogenic radionuclides were low and far below the adopted dose reference level of 1 mSv/yr (ICRP, 2012). The most prominent contributor to the dose was the UB mean exposure estimate for ^{241}Am. The dose coefficient for ^{241}Am is high due to its propensity to bind to bone surfaces after absorption, which results in a long residence in the body. In certain exposure settings, for example in the vicinity of some nuclear facilities some environmental exposure to ^{241}Am may occur (CEFAS, 2014). However New Zealand has no nuclear facilities. The major non-nuclear occurrence of ^{241}Am is in the detectors of smoke alarms. Here the ^{241}Am is in a sealed source which is expected to remain intact through use and landfill disposal. It would be highly unlikely to enter the food chain, and as such the UB mean estimate of dose from ^{241}Am is conservative for New Zealand. As no ^{241}Am activity was detected in any foods in Chapter Two, the upper-bound exposure estimate is based on calculation from the assay minimum detectable concentrations (MDCs). In Chapter Two ^{241}Am activity was analysed by its gamma emission spectra which are not able to obtain very low MDCs. Analysis of ^{241}Am can also be undertaken through alpha spectrometry which gives a higher degree of sensitivity and much lower MDCs. As reported in Section 2.3.5. this method was used to assay for the other transuranic nuclides $^{239+240}$Pu with no resulting detects. UNSCEAR records that global atmospheric release from nuclear testing of ^{241}Pu, the parent of ^{241}Am, was greater than 10 times that of $^{239+240}$Pu (142 PBq against 10.8 PBq; UNSCEAR, 2000). The 14.4 years half-life of ^{241}Pu means that decay to ^{241}Am is gradual and that the environmental inventory is unlikely to peak until 2035 (ATDSR, 2004). Despite this many studies of soils, sediments and waters effected by nuclear fallout have shown generally

higher environmental ratios of $^{239+240}$Pu to ^{241}Am (Lusa et al., 2009; Irleweck & Hrnecek, 1999).

There are few studies available that record the co-occurrence of $^{239+240}$Pu and ^{241}Am in the diet. The UK Radioactivity in Food and the Environment (RIFE) study details activities for $^{239+240}$Pu and ^{241}Am around several nuclear institutions. Between 2004-2014 activity concentrations of $^{239+240}$Pu and ^{241}Am in seafood around the Sellafield discharge were generally closely related (CEFAS, 2014). Notably a study of radionuclides depositing in bone in surgery patients, from a background level area in Poland, gave very comparable activity concentrations for $^{239+240}$Pu and ^{241}Am suggesting exposure to these radionuclides over a lifetime is similar (Mietelski et al., 2011). Considering these factors it was judged unlikely that ^{241}Am would be present in the New Zealand diet at activity concentrations in excess of $^{239+240}$Pu. As a result a second dose calculation was undertaken replacing the UB mean exposure for ^{241}Am with the MDCs obtained for $^{239+240}$Pu via alpha spectrometry. This second estimate for ^{241}Am resulted in a reduction by a factor of 20-25 in the estimated dose range and is considered more realistic for New Zealand (Table 3.4.).

Considering the historical monitoring data for anthropogenic ^{137}Cs and ^{90}Sr in milk there is strong evidence that the contribution from anthropogenic radionuclides to the dietary dose has decreased considerably over the last 50 years. A dietary dose can be calculated solely from the mean New Zealand milk activities for ^{137}Cs and ^{90}Sr in 1965 (33.2 and 5.6 Bq/kg respectively) (Matthews, 1993). Using the consumption values calculated in the current work (Table 3.2.) the annual dose from milk alone would have been 84.7 μSv for an adult male and 59.4 μSv for a 5 year old child. Both values are approximately 5 fold higher than the current upper-bound estimated dose for anthropogenic radionuclides across the diet.

Assuming the cessation of any further nuclear inputs it is possible to calculate a conservative estimate of the dietary dose from ^{137}Cs and ^{90}Sr 50 years into the future. Using the established half-lives for both radionuclides the activity concentrations found in Chapter Two can be decay adjusted to 2065. A limitation is the assumption that other environmental process that remove the radionuclides from the food chain do not occur which would further lower activities. The forecasted annual dose from ^{90}Sr and ^{137}Cs for an adult in 2065 using the UB means would be 1.57 μSv. The forecasted reduction is relatively minor in comparison to the decrease over the previous 50 years.

Potassium in the human body is under homeostatic control, and thus while it is readily absorbed from the diet and distributed to all organs in the body, a proportion is then rapidly excreted to keep body levels in equilibrium. Due to the slow decay rate of ^{40}K its natural ratio to stable potassium will not change to a significant extent over a human lifespan. Therefore if the ratio remains unchanged there is a near constant lifetime dose rate from ^{40}K regardless of activity concentrations present in the diet. UNSCEAR notes that the calculated annual dose for adults from ^{40}K is 165 μSv/yr and that calculated for children is 185 μSv/yr (UNSCEAR, 1993). As a result of the estimated dose from ^{40}K being independent from dietary activities of this isotope the dose calculated from ^{40}K activities in the sampled foods was omitted from further calculations.

The largest contribution to the estimated dose, particularly in adult males, results from ^{210}Po. This is a consequence of high consumption of fish and shellfish. In comparison, of the other NORM radionuclides, the radiological burden from dietary uranium is low across all the age/gender groups. UNSCEAR has published global reference values for committed dose to the different age groups for the ^{238}U decay series radionuclides analysed, and also ^{235}U (UNSCEAR, 2000). The reference values are

generally comparable to those calculated in this chapter (Table 3.5.). For adult males the dose from ^{210}Po is greater, however, likely as a result of higher seafood consumption in the New Zealand adult male population relative to other countries.

Table 3.5. Comparison of the annual committed dose through ^{210}Po and uranium isotopes in the New Zealand diet against the estimated global average (UNSCEAR, 2000).

Population group	Mean dietary radionuclide exposure (μSv/yr)			
	^{238}U	^{234}U	^{210}Po	^{235}U
Adult male -NZ	0.45-0.50	0.40-0.71	124.23-134.33	0.0002-0.27
Adult female -NZ	0.34-0.38	0.30-0.53	68.09-74.81	0.0002-0.21
Adult -Global	0.25	0.28	70	0.012
Child –NZ	0.31-0.34	0.40-0.52	61.57-76.85	0.0002-0.13
Child -Global	0.26	0.28	100	0.012
Infant –NZ	0.30-0.32	0.44-0.54	76.89-102.24	0.0002-0.15
Infant –Global	0.23	0.25	180	0.011

The total UB mean dose for adult males was examined with respect to contributing radionuclide (Figure 3.1.) A range of naturally occurring radionuclides, apart from ^{210}Po and $^{234+235+238}$U, are present in the environment, including other members of the uranium decay series, thorium series radionuclides and other primordial or cosmogenic non-series radionuclides. These radionuclides were not analysed for in the foods tested in Chapter Two, however published estimates can be used to estimate likely contribution. Most significant are ^{210}Pb (21-40 μSv/yr) and radium-228 (^{28}Ra; 11-40 μSv/yr) (UNSCEAR, 2000). Potential dietary doses of ^{226}Ra and ^{228}Ra through some horticultural commodities and animal products are estimated in Chapter Six.

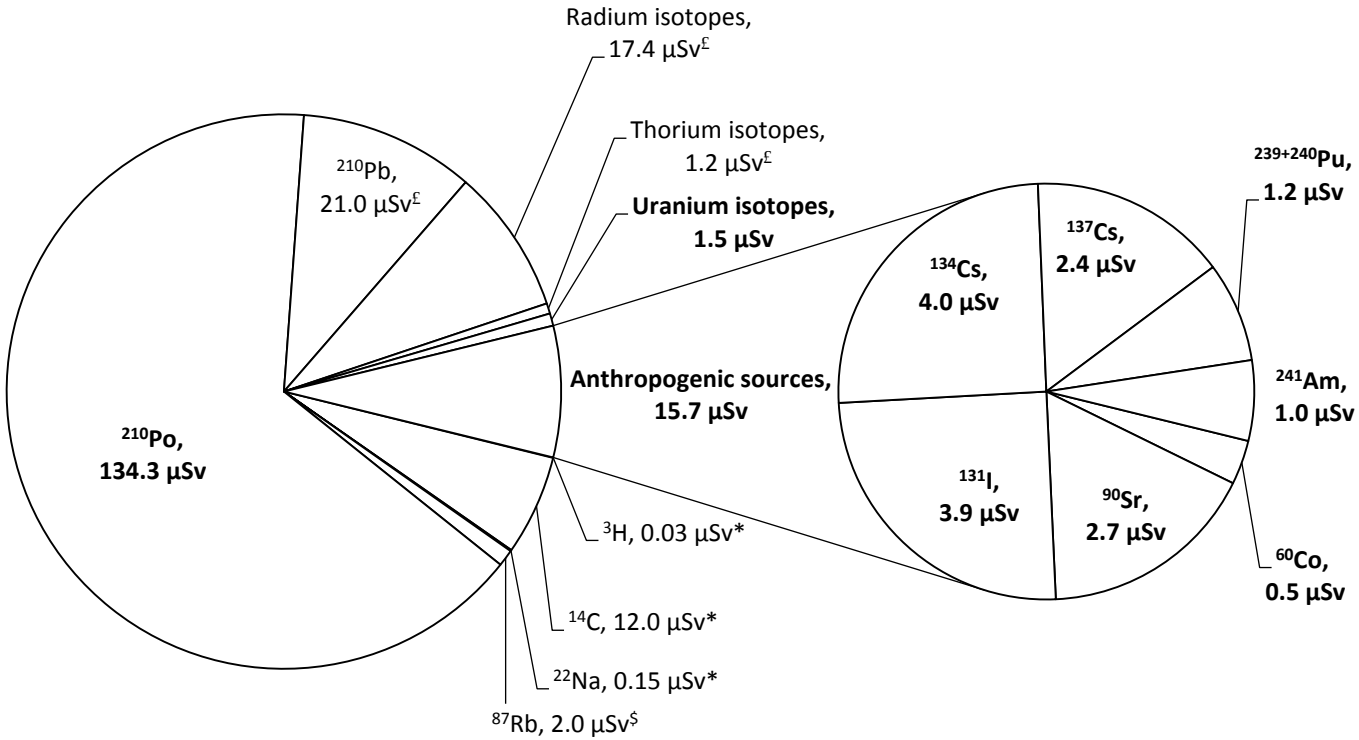


Figure 3.1. Contributors to annual ingested dose for an adult male (≥25 yrs) from dietary radionuclides, Bolded values are calculated from upper-bound mean activity concentrations obtained in New Zealand foods in Chapter Two. Excluding the fixed dietary dose contribution resulting from ^{40}K (UNSCEAR, 1993)

Sources: $ Watson et al., 2005, * UNSCEAR, 1993, £ UNSCEAR, 2000.

When calculating exposure based on the UB means, for all of the age/gender groups, the naturally occurring radionuclides from the ^{238}U and ^{232}Th series represent greater than three quarters of the contribution. The remaining contribution is from anthropogenic sources and other primordial and cosmogenic radionuclides. Undertaking the calculation with the LB means, for all of the age/gender groups, results in the contribution from anthropogenic sources reducing to less than 1% of the total dose, of which the majority results from ^{137}Cs.

The large contribution to the total dose from ^{210}Po is a consequence of its higher activities in foods and the greater dose resulting from each decay. Similar findings are reported from overseas. In a 2008 study in Japan ^{210}Po exposure led to a contribution of 0.73mSv, which accounted for 91% of the dietary dose (Ota et al., 2009). In certain cases, such as in uranium rich regions, contributions from ^{210}Po and ^{210}Pb can be very large. In a uranium-bearing region of Cameroon an ingestion dose of 2 mSv was calculated from the ^{238}U and ^{232}Th decay series activities in the diet (Saïdou, 2011). Of this dose 62% resulted from the ^{210}Po activities and 36% from the ^{210}Pb activities.

In assessing contributions to exposure it can be valuable to understand the proportion of dose arising from certain food types in the diet. There are marked differences between proportions of each food group to the total dietary dose for each age group (Figure 3.2.). For adult males the dose through seafood, primarily that resulting from ^{210}Po, made up more than two thirds of the total exposure. This is explained by this age/gender group having the highest fish and shellfish consumption. As ^{210}Po was present in the majority of seafood species analysed in Chapter Two, very little difference in contribution was seen between LB and UB activities. The high contribution from seafood matches the results of a study in Japan in which seafood contributed 80% of the dose (Ota et al., 2009). The

contribution of seafood decreased for the other age/gender groups, especially in children and toddlers, due to the reduced fish and shellfish consumption in these age groups. In all of the age groups vegetables contribute a low proportion to total dose. Contributions for children and toddlers were more evenly distributed across the different food groups, confirming that in the absence of the higher activities in seafood, activities of most of the radionuclides were approximately the same between the other food types. The finding of shifting age/gender-related doses differs to the results of an Italian study of exposure resulting from ^{210}Po activity in the diet, where the proportional contribution from each source was relativity constant through different age groups (Meli et al., 2014).

3.3.2. Semi-probabilistic dietary dose assessment

Semi-probabilistic modelling offers the opportunity to examine exposure patterns across a representative population as provided by a national nutrition survey. The 08ANS encompassed 4721 adult respondents aged 15+ years (University of Otago & MOH, 2011). The 02CNS covered 3275 New Zealand children between 5 and 14 years of age (MOH, 2003). By assigning the activity concentrations of all the radionuclides against the respondent data from both surveys it was possible to provide an estimate of the likely ranges of dose the population receives each day from consumption patterns. As the modelling incorporates a large consumption dataset it is more realistic in estimating exposure across a population than a deterministic model.

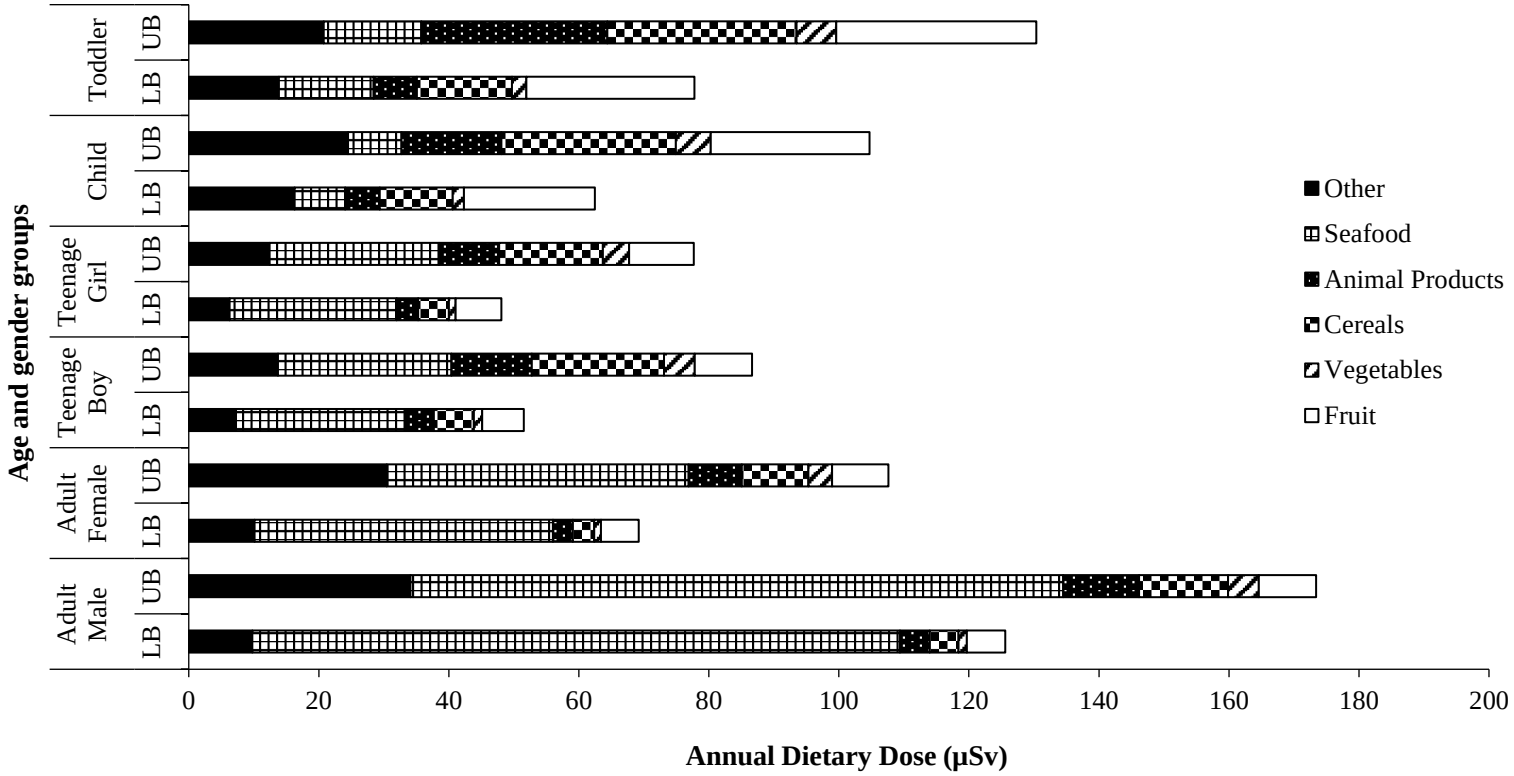


Figure 3.2. Contribution of different food groups to upper-bound (UB) and lower-bound (LB) annual ingested doses for each age and gender grouping.

Note: Excludes ^{40}K and with UB ^{241}Am activities adjusted to the minimum detectable concentration values for $^{239+240}Pu$.

Semi-probabilistic dietary exposure models were run for all UB and LB mean activity concentrations of each of the food types collected in Chapter Two against the latest New Zealand adult and child nutrition survey respondents (MOH, 2003; University of Otago & MOH, 2011). The model established UB and LB daily committed doses at different percentiles of the survey respondent populations and mean daily and annual doses (Table 3.6).

Table 3.6. Estimated percentiles of daily ingested ionising radiation dose and calculated mean population annual dose following semi-probabilistic modelling of participants from two New Zealand Nutrition surveys. Using upper-bound(UB)and lower-bound (LB) mean activities.

	Daily committed dose at n^{th} percentile of survey population (LB-UB) (µSv/person/day)						**Mean annual committed dose (LB-UB) (µSv/person/yr)**
Survey	**2.5**	**10**	**50**	**90**	**97.5**	**Mean**	
2008 ANS	0.006-0.03	0.01-0.04	0.03-0.09	0.31-0.37	1.39-1.44	0.17-0.22	62.1-80.4
2002 CNS	0.02-0.07	0.04-0.10	0.10-0.21	0.32-0.47	1.75-1.84	0.25-0.35	91.3-127.8

Based on the mean calculated daily intake an annual dose of between 62-80 µSv/yr for an adult and 91-128 µSv/yr for a child (Table 3.6.) was calculated. These values support those calculated through the deterministic modelling. Also similar to the results of the deterministic modelling, the survey respondent diets containing fish or shellfish contributed to daily doses at the highest end of the population range. For example, in adults consuming cod on the day of the nutrition survey, at a mean intake amount of 216 g/person/day, the ingested dose was 0.95 µSv/day. This supports the identification of seafood consumers as being a significant exposure group. Further research on exposure of high seafood consumers to radionuclides is presented in Chapter Four.

The results of both deterministic and semi-probabilistic models indicate that on a population basis exposures to radionuclides in the New Zealand food supply are low. The absence of significant contribution from anthropogenic radionuclides can be explained by New Zealand's relative isolation from nuclear testing and nuclear accidents, and the lack of any domestic nuclear industry. Some degree of anthropogenic radionuclide contamination is possible on a localised scale as has been demonstrated by the detection in Chapter Two of ^{131}I of medical origin in New Zealand shellfish samples. The significance of this temporary and localised contamination to human health is likely to be low given the large margin between current anthropogenic exposures and the reference dose level. Additionally, the import of foods with anthropogenic radionuclides falling within the Codex Alimentarius guidelines is also unlikely to add a significant burden to the dietary dose.

Due to the significance of uranium decay series radionuclides as part of the naturally occurring dose, identification of increases from this contribution is important. An increase of NORM as a result of concentration processes and release from industry can lead to a significant increase in the committed dose. Because of the potential for the release of TeNORM to occur outside of the nuclear industry, in the absence of a significant regional nuclear release, it is considered that an increased dose from TeNORM represents the greatest dietary radiological risk to the New Zealand population. Chapter Six details the examination of the future risks of a current source of TeNORM input to New Zealand agriculture.

3.3.3. Uranium chemical exposure

A deterministic exposure assessment for uranium's chemical toxicity was undertaken using the same dietary mapping as used for the deterministic dose assessment (Table 3.7.). As natural uranium on a mass

basis is predominantly ^{238}U, only this value has been used to derive the uranium chemical mass concentration present across the diet.

The dietary exposure to uranium represented only a low proportion of the WHO TDI for all age ranges, falling between 2 and 8%, with the highest estimated exposure being in toddlers and the lowest in teenage girls (Table 3.7.). Due to the changing diets between age groupings and approximately the same uranium concentrations across most of the foods, the primary contributors to the exposure differed between the age groupings. For adults, coffee and beef steak were the principal sources of exposure. For teenagers and children the contribution to exposure was from all food sources, although pasta and milk increased in importance as the proportion of these in the diet increased. Soluble uranium is an important contaminant to consider in drinking water (EFSA, 2009). However, based on its exposure contribution of less than 1% of the WHO TDI, uranium from New Zealand bottled and artesian waters it is unlikely to represent a concern to New Zealand public health. The chemical exposure estimates for uranium in the New Zealand diet are comparable to those published overseas, and also fit the global reference value of approximately 3% of the WHO TDI (Garcia et al., 2006; Jha et al., 2012; UNSCEAR, 2000).

Table 3.7. Uranium dietary burdens for different age/gender groups of the New Zealand population as a percentage of the WHO TDI. Characterised by food group using upper-bound (UB) and lower-bound (LB) mean uranium concentrations.

Food Group	Mean uranium exposure (%WHO TDI)					
	Adult male (82 kg) LB-UB	**Adult female (70 kg) LB-UB**	**Teenage boy (54 kg) LB-UB**	**Teenage girl (55 kg) LB-UB**	**Child (23 kg) LB-UB**	**Toddler (13 kg) LB-UB**
Fruit	0.18-0.20	0.22-0.26	0.13-0.16	0.13-0.17	0.35-0.45	0.45-0.57
Vegetables	0.08-0.25	0.09-0.21	0.10-0.31	0.07-0.26	0.10-0.39	0.12-0.40
Cereals	0.87-0.91	0.69-0.73	1.20-1.28	1.13-1.20	2.06-2.19	2.69-2.81
Animal Products	1.11-1.17	0.89-0.92	1.57-1.62	1.11-1.15	1.89-1.97	2.04-2.10
Seafood	0.30	0.18	0.14	0.11	0.12	0.15
Other	1.44-1.60	1.44-1.64	0.43	0.39-0.40	0.83-0.85	0.72
Total	3.98-4.42	3.51-3.94	3.57-3.94	2.95-3.28	5.35-5.98	6.18-6.76
Total scaled diet	4.53-5.03	3.97-4.46	4.24-4.68	3.49-3.88	6.19-6.91	6.98-7.64

3.4. Conclusion

Using both deterministic and semi-probabilistic models, has provided estimates of the committed dose from radionuclide activities in the food chain to the New Zealand population. Contribution of anthropogenic radionuclides to total dose was low to negligible and estimated as being far below the reference dose level of 1 mSv/yr. This dose has decreased considerably since the height of atmospheric nuclear testing but is unlikely to continue to decrease at the same rate. Naturally occurring radionuclides contributed significantly to the committed dose, with ^{210}Po being predominant amongst these, in particular through its presence at

significant levels in seafood. Total estimated doses for all age and gender groups fell within the expected global range and indicate that the risk to the New Zealand population is low. Modelling dose across two survey populations indicates a large variation in the daily dose between consumers, with seafood consumption leading to highest daily doses.

Chemical exposure risks to uranium have also been assessed using the deterministic model. The results of this modelling indicate that the New Zealand population is exposed to less than 10% of the WHO TDI and the exposure risk is negligible.

The results of this chapter indicate that the current ranges of activities of radionuclides present in the New Zealand diet are not a cause for concern. The determination of the committed population doses for New Zealand allows for risk assessments to be undertaken in the event of an emergency or due to an increased trend of exposure to determine the significance to health.

Chapter 4 - Activity concentrations of caesium-137 and polonium-210 in seafood from fishing regions of New Zealand and the dose assessment for seafood consumers.

4.1. Introduction

With 15000 km of coastline and a 6.7 million km^2 Exclusive Economic Zone (EEZ), respectively the tenth and sixth largest of any country in the world, the marine environment is a significant and valuable resource for the New Zealand population (Coriolis, 2014). Seafood is collected and harvested on various scales, with a number of quota management systems in place and certain marine species, including Hoki and Rock lobster, have significant value in terms of trade. Seafood has importance to the New Zealand population as a source of nutrition and is consumed in considerable amounts by some sectors of the community (Tipa et al., 2010; Turner et al., 2005). Fisheries are also a traditional source of sustenance, economic wealth and cultural wealth for whānau, hapū and iwi. Being able to provide fish or shellfish to feed whānau (family) or manuhiri (guests) has always been part of the cultural heritage of tangata whenua. Historically many of the inshore finfish and shellfish species found throughout the different coastal regions formed a staple part of the early Māori diet and are viewed as taonga (Tipa et al., 2010). Chemical contaminants in seafood can therefore lead to significant health burdens to the population and it is an important public health function to identify contaminants of concern and characterise their exposure.

The presence of radionuclides in the environment has been of significant global concern over the last half century. Following the recent accident at the Fukushima Daiichi Nuclear Power Plant, concern has been raised regarding the potential impact of radionuclide release into the Pacific Ocean on seafood, and consequently seafood consumers.

Chapter based on: Pearson, A.J., Gaw, S., Hermanspahn, N., Glover, C.N., 2016. Activity concentrations of ^{137}Caesium and ^{210}Polonium in seafood from fishing regions of New Zealand and the dose assessment for seafood consumers. Journal of Environmental Radioactivity, 151:3, 542-550.

Radionuclide monitoring of the marine environment surrounding New Zealand has been limited to date. A much greater focus has been placed on identifying and quantifying terrestrial fallout, through atmospheric dry and wet deposition and through monitoring milk powders from various regions of the country (Matthews, 1993).

Global release of anthropogenic radionuclides from nuclear weapons testing has also contributed to the levels of radionuclides in the environment. Historically, for the Southern Hemisphere the most significant contributor to marine anthropogenic radionuclide activities has been nuclear weapons testing. Direct input of global fallout into the South Pacific Ocean (S 30º-60º) has been calculated at 25.8 PBq and 41.3 PBq for ^{90}Sr and ^{137}Cs respectively (IAEA, 2005). Oceanic anthropogenic radionuclide activities for four latitudinal boxes of the Pacific and Indian Ocean surrounding New Zealand were estimated for the start of the millennium as being 0.4-0.8 Bq/m^3 for ^{90}Sr and 0.6-1.4 Bq/m^3 for ^{137}Cs (Povinec et al., 2004).

With the input of a significant inventory of radionuclides from the Fukushima-Daiichi nuclear accident into the Northern Pacific, concerns have been raised in many countries surrounding the Pacific as to the potential increase in risks that may result. Modelling of the oceanic distribution suggests that ^{137}Cs from Fukushima-Daiichi will elevate Tasman Sea and Southwest Pacific radionuclides by 0.01 Bq/m^3 by 2026, with continuing dispersion through the region over the subsequent 15 years (Nakano & Povinec, 2012).

Certain NORM including ^{238}U and its decay series are present in the marine environment through natural processes, such as terrestrial influx from atmospheric deposition or fluvial transport. As certain minerals can have higher abundances of NORM than are generally present in the crust, the extraction, processing and utilisation of these deposits can lead to

concentration of NORM. This technological enhancement of NORM presents a risk for radionuclide entry into the environment from a number of industries which do not involve nuclear technology or nuclear fuel extraction (UNSCEAR, 2000).

The survey of radionuclides across the New Zealand diet in Chapter Two included the muscle tissue of three fish species and three shellfish species for levels of anthropogenic and naturally occurring radionuclides. Of the radionuclides surveyed ^{137}Cs and ^{210}Po were found mainly in seafood species. ^{137}Cs activity was consistently detected in the higher trophic level fish but was absent in shellfish, while ^{210}Po showed greater variation, with considerably higher levels in shellfish and a roughly hundred-fold difference between tuna and lemonfish. ^{234}U and ^{238}U activities were present in all samples, with significant activities in shellfish, but did not show any elevation in the finfish species over that of terrestrial food sources.

Given the range and magnitude of radionuclides present in seafood monitoring of radionuclides in the seafood species may be necessary to provide a complete and accurate portrayal of dietary radionuclide exposure in the New Zealand population. Such an undertaking would complement the current milk monitoring program for terrestrial contamination (Hermanspahn, 2010). To support a seafood monitoring programme, additional research is necessary to better characterise the ranges, and any regional differences, of radionuclides in various New Zealand seafood species including through establishing suitable sentinel radionuclides for monitoring long term trends. The recorded ^{137}Cs and ^{210}Po activities in the analysed seafood samples from Chapter Two highlight their suitability as marine monitoring sentinels. ^{137}Cs is a representative anthropogenic radionuclide, with properties such as; significant fission yield, high mobility in the environment and potential

for uptake in the marine food chain. ^{210}Po is a marker for NORM sources and also displays the potential for high uptake levels in seafood species. Developing a dataset for ^{137}Cs and ^{210}Po in seafood will also provide a more refined estimate of ionising radiation exposure within seafood diets.

This chapter details the monitoring program for ^{137}Cs and ^{210}Po activities in seafood, outlining the sampling from different fishing regions of New Zealand and interpreting the results in the context of the expected behaviour of the radionuclides in the marine environment. Finally, the outcome of dose assessment models for seafood consumers is presented. The objective of this chapter is to establish the significance of radionuclide activity levels in seafood as a near to mid-term risk to food security.

4.2. Materials and methods

4.2.1. Sampling methodology

The EEZ of New Zealand is divided into ten general fishery management regions (Figure 4.1.). In order to obtain a wide geographic distribution, the boundaries of these regions were utilised to classify samples as occurring from different sections of the New Zealand coastline. The sampling protocol was designed to capture a range of key seafood species and also analyse for differences between ecological niches.

In addition to targeting niche-specific species in each management region (see sampling protocol in Table 4.1.), two species were specifically targeted as being important commercial catch species for New Zealand. These were the teleost fish, hoki (*Macruronus novaezelandiae*), and the cephalopod mollusc, arrow squid (*Nototodarus* spp. - *N. gouldi, N. sloanii*). These are deep water species with well-defined fishing stock areas.

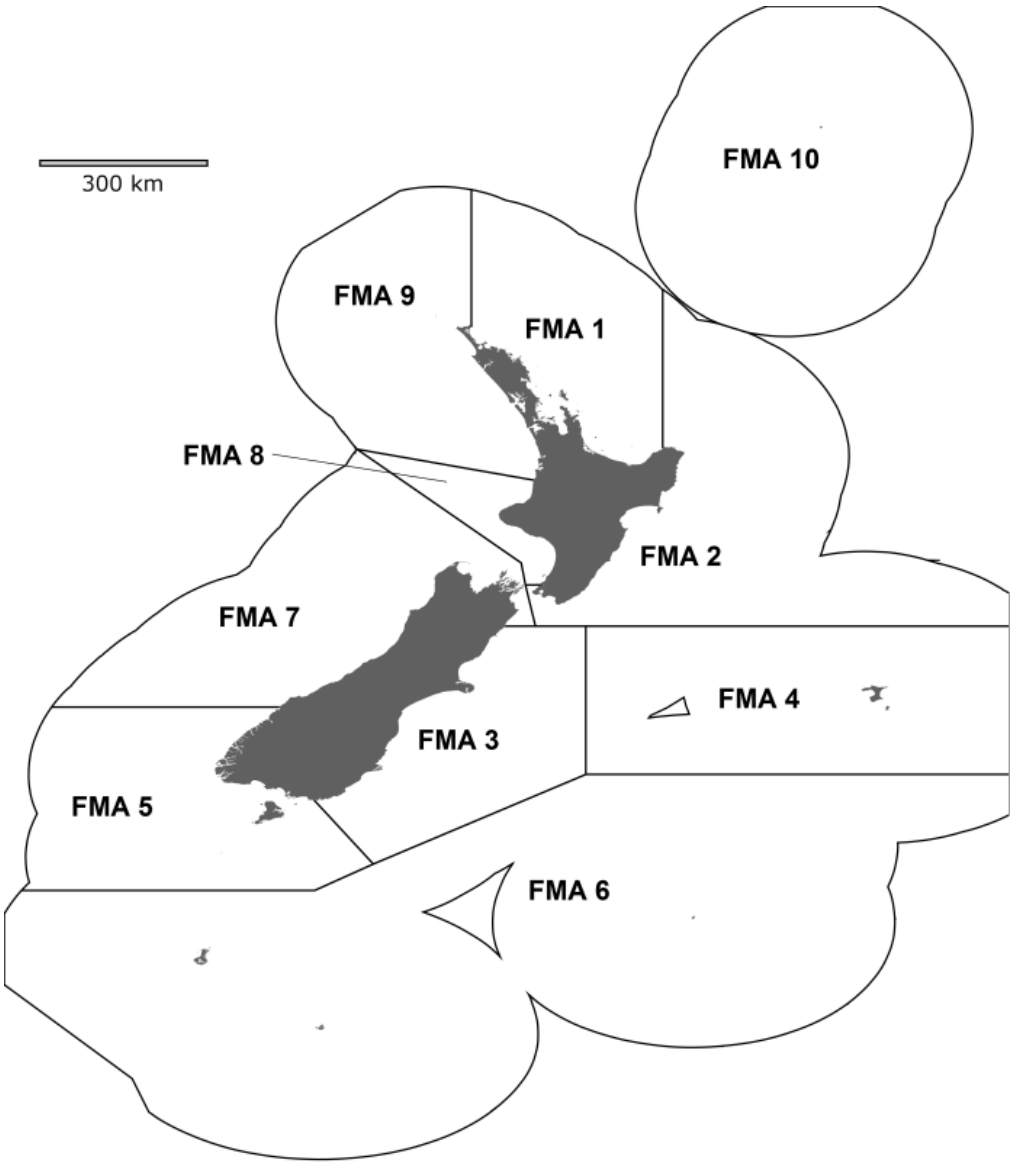


Figure 4.1. Outline of New Zealand General Fisheries Management Areas (FMA).

Source: Adapted from MPI, 2014.

All samples specified in the protocol were obtained through commercial suppliers, with additional Rock lobster and Bluff oyster samples also supplied from the Southland fishing region. The coastal pelagic fish was tarakihi (*Nemadactylus macropterus*) which was able to

be collected from each coastal fishery region. The full details of the species sampled from each region are listed in Table 4.1. A minimum of 140 g of edible tissues was supplied for each species and the date and region of harvest recorded.

4.2.2. Sample preparation and analysis

Samples were received chilled or frozen and allowed to thaw prior to homogenisation. Fish samples consisted primarily of muscle, with the majority of skin and large bones removed. Crustacean samples were prepared by removing inedible exoskeleton and any non-edible organs prior to homogenisation. For rock lobster this included removing hepatopancreas, which although is consumed, provided insufficient mass to meet analytical requirements. Kina were sampled as pre-removed gonads. Molluscs (excluding the squid) were removed from shells and homogenised. All samples were frozen prior to gamma spectroscopy to delay microbial spoilage during counting.

Samples were transferred to clean 400 ml cylindrical containers and analysed for gamma emissions using CANBERRA high purity germanium semiconductor detectors. Samples were counted for a minimum of 48 hours. All spectra were analysed to derive emission counts for ^{134}Cs and ^{137}Cs (Appendix A, Figure A.3.). Activity concentrations of any other anthropogenic gamma-emitting radionuclide were recorded if present, and activity concentrations of ^{210}Pb were recorded if above the MDC calculated for each assay.

A 5 g fresh weight sub-sample of each homogenised sample was used for the ^{210}Po assay. ^{210}Po sample preparation and analysis were undertaken using the methodology in Section 2.2.4. Activity concentrations for ^{210}Po were compared against any detectable activity concentrations of ^{210}Pb to determine the proportion supported and unsupported in each sample.

Table 4.1. Seafood sampling protocol, with samples obtained, from New Zealand fishing regions for analysis of radionuclide content.

Fishery regions	Target Species	Sampled species[a]
Auckland and Kermadec (FMA1, FMA9, FMA10)	Oceanic pelagic fish	Skipjack tuna
	Coastal pelagic fish	Tarakihi
	Demersal fish	Snapper
	Non-molluscan invertebrate	Rock lobster
	Mollusc	Greenshell mussels
Central (FMA2)	Oceanic pelagic fish	Southern bluefin tuna
	Coastal pelagic fish	Tarakihi
	Demersal fish	Red cod
	Non-molluscan invertebrate	Rock lobster
	Mollusc	Paua
South East (FMA3 FMA4)	Oceanic pelagic fish	Orange roughy
	Coastal pelagic fish	Tarakihi
	Demersal fish	Flounder
	Non-molluscan invertebrate	Rock lobster
	Mollusc	Queen scallop
Southland (FMA5)	Oceanic pelagic fish	School shark
	Coastal pelagic fish	Tarakihi
	Demersal fish	Blue cod
	Non-molluscan invertebrate	2x Rock lobster
	Mollusc	2x Bluff dredge oyster
Challenger/ Central (Egmont) (FMA7, FMA8)	Oceanic pelagic fish	Albacore tuna
	Coastal pelagic fish	Tarakihi
	Demersal fish	Ling
	Non-molluscan invertebrate	Kina
	Mollusc	Littleneck clams
Sub Antarctic (FMA6)	3 Oceanic pelagic or demersal fish	Southern blue whiting 2x Ling
Specific stock area	Hoki	3x Hoki
	Squid	3x Arrow squid

[a] Binominal names: Albacore tuna (*Thunnas alalunga*); Arrow squid (*Nototodarus spp. - N. gouldi, N. sloanii*); Blue cod (*Parapercis colias*); Bluff dredge oyster (*Tiostrea chilensis*); Flounder (*Rhombosolea leporine*); Greenshell mussels (*Perna canaliculus*); Hoki (*Macruronus novaezelandiae*); Kina (*Evechinus chloroticus*); Ling (*Genypterus blacodes*); Littleneck clams (*Austrovenus stutchburyi*); Orange roughy (*Hoplostethus atlanticus*); Paua (*Haliotis iris*); Queen scallop (*Zygochlamys delicatula*); Red cod (*Pseudophycis bachus*); Rock lobster (*Jasus edwardsii*); School shark (*Galeorhinus australis*); Skipjack tuna (*Katsuwonus pelamis*); Snapper (*Chrysophrys auratus*); Southern bluefin tuna (*Thunnus maccoyii*); Southern blue whiting (*Micromesistius australis*); Tarakihi (*Nemadactylus macropterus*).

4.2.3. Data analysis

Emission counts for both isotopes were calculated using the CANBERRA Genie 2000 program. If sufficient activity was present for an isotope, a method error based on 2 standard deviations was reported. Trace activity concentrations below the MDC can be detected but not quantified with absolute certainty. For such samples the indicative value reported was deemed a trace result. A large proportion of non-detect results complicates the calculation of arithmetic mean activities. To identify the likely ranges of ^{137}Cs mean activities, these have been reported as both lower-bound (LB), whereby all non-detect values were assigned a value of zero, and upper-bound (UB), where all non-detect values were assigned the value of the assay MDC. Trace results were included at the reported value for calculating both UB and LB means. For ^{210}Po all samples had detected or indicative trace activity concentrations and thus means were calculated from all values. Statistical analysis was conducted using the Mann-Whitney *U* test to analyse for differences between species from different ecological niches, and to test for differences between species from different regions. This allowed the exploration of the hypothesis that these variables (niche and region) lead to populations with larger activity concentrations.

4.2.4. Dose assessment for high seafood consumers

To determine the exposure associated with a high or subsistence seafood consumption diet, a high diet model consisting of consumption by an individual of 300 g finfish, 200 g crustacean or squid and 100 g molluscs a week was used. These values were calculated from the mean daily consumption amounts in the 2008 Adult National Nutrition Survey of marine fish (82 g/person), squid (40 g/person) and molluscs (29 g/person) (University of Otago & MOH, 2011). Each commodity was conservatively estimated as being consumed four times over a week, with

values rounded to the nearest 100 grams. A model was developed in Microsoft Excel 2007 to randomly assign the activity concentrations of one of the samples of each group analysed in the seafood survey to each of the fifty two weeks of a year. A further fully probabilistic model randomly assigned a weekly dietary consumption of between 0 and 1000 g of each of the three seafood types.

Both models then derived an annual dose estimate by summing the total activities and converting through the International Commission on Radiological Protection (ICRP) established dose conversion factors for an adult (^{137}Cs: 0.013 μSv/Bq, ^{210}Po: 1.2 μSv/Bq; ICRP, 2012). The models were run for 10,000 iterations for both the ^{137}Cs and ^{210}Po seafood analytical datasets. Exposure estimates at the 5th, 25th, 50th, 75th, 95th and 99th percentiles were then calculated.

4.3. Results and discussion

4.3.1. Gamma spectroscopy

All 36 seafood samples underwent gamma spectroscopy to determine ^{134}Cs and ^{137}Cs activity concentrations. The analysis of ^{137}Cs in New Zealand fish in Chapter Two had indicated that activity concentrations were generally at a trace level. As such there was a requirement to obtain low MDCs in the region of 0.1-0.2 Bq/kg to determine the presence of ^{137}Cs. This was primarily achieved by using large analytical masses of 200-500 g and long counting times. Following analysis, all samples had interpretable spectra, which were utilised to calculate activities for ^{134}Cs and ^{137}Cs, and derive MDCs. None of the samples had detectable activity concentrations of ^{134}Cs. Seventeen of the 36 samples analysed had detectable ^{137}Cs activity concentrations. However, of these only two samples had activity concentrations exceeding the assay MDC. The remaining 15 recorded trace activity concentrations for ^{137}Cs, denoting that the isotope was present but the reported value was indicative only.

Detected activities, with associated standard error at 95% confidence, and assay MDCs are reported in Table 4.2.

Detection of ^{137}Cs occurred in all the fishing regions, and of the samples tested was most common in the finfish, with some noted exceptions. Consistent with the absence of ^{137}Cs in shellfish reported in Chapter Two, invertebrates (including squid and shellfish) did not show any ^{137}Cs activity. The sole exception was a single oyster and rock lobster sampled from Southland. The other oyster and rock lobster samples obtained from the Southland fishing region did not have detectable ^{137}Cs activity concentrations. UB and LB means and ranges for each of the ecological niches were calculated (Table 4.3.).

Table 4.2. ^{137}Cs and ^{210}Po activity concentrations ± standard error at 95% confidence, with assay MDCs for 36 samples of seafood.

Fishery region	Sampled species	^{137}Cs (Bq/kg ww)		^{210}Po (Bq/kg ww)	
		Activity	MDC	Activity	MDC
Auckland and Kermadec	Skipjack tuna	0.107±0.043	0.147	32.77±2.29	0.08
	Tarakihi	0.090±0.043	0.135	2.90±0.50	0.15
	Snapper	ND	0.113	0.31±0.16	0.13
	Rock lobster	ND	0.171	0.71±0.24	0.12
	Greenshell mussels	ND	0.081	11.33±1.15	0.06
Central	SBT[a]	0.125±0.035	0.132	1.11±0.28	0.11
	Tarakihi	ND	0.109	1.07±0.36	0.21
	Red cod	0.052	0.073	0.21±0.14	0.11
	Rock lobster	ND	0.126	0.11±0.13	0.21
	Paua	ND	0.133	2.71±0.47	0.09
South East	Orange roughy	ND	0.110	0.05±0.07	0.13
	Tarakihi	0.069	0.141	1.44±0.38	0.12
	Flounder	ND	0.094	6.00±0.83	0.08
	Rock lobster	ND	0.216	0.28±0.12	0.07
	Queen scallop	ND	0.101	283.54±15.89	0.11
Southland	School shark	0.213±0.055	0.150	0.08±0.08	0.10
	Tarakihi	ND	0.185	1.87±0.38	0.09
	Blue cod	0.145	0.202	0.48±0.18	0.09
	Rock lobster	ND	0.118	2.09±0.37	0.09
	Rock lobster	0.088	0.169	1.50±0.33	0.11
	Bluff oyster	ND	0.079	98.31±5.80	0.09
	Bluff oyster	0.153	0.213	71.82±4.37	0.07
Challenger/ Central (Egmont)	Albacore tuna	0.144±0.052	0.133	1.32±0.37	0.09
	Tarakihi	0.060	0.088	2.71±0.57	0.18
	Ling	0.104±0.047	0.138	0.17±0.13	0.12
	Kina	ND	0.057	2.40±0.79	0.31
	Littleneck clams	ND	0.095	21.89±1.62	0.09
Sub Antarctic	SBW[b]	ND	0.167	0.96±0.35	0.15
	Ling	0.068	0.115	0.24±0.16	0.16
	Ling	0.068±0.041	0.104	0.38±0.19	0.14
Specific stock area	Hoki	0.126±0.049	0.128	1.91±0.37	0.05
	Hoki	0.052	0.108	0.77±0.29	0.14
	Hoki	0.092±0.048	0.179	1.20±0.30	0.06
	Arrow squid	ND	0.122	1.33±0.74	0.34
	Arrow squid	ND	0.189	2.22±0.97	0.35
	Arrow squid	ND	0.159	2.30±0.96	0.60

ND: Not detected; [a] SBT: Southern bluefin tuna; [b] SBW: Southern blue whiting.

Table 4.3. Upper bound (UB) and lower bound (LB) mean ^{137}Cs activity concentrations and ^{210}Po mean activity concentrations with standard deviation for 36 samples of New Zealand seafood.

Ecological niche/ species	Mean ^{137}Cs LB:UB (Bq/kg ww) (range)	Mean ^{210}Po ± SD (Bq/kg ww) (range)
Oceanic pelagic fish	0.10-0.14 (0.11-0.21)	6.05±13.10 (0.05-32.77)
Coastal pelagic fish	0.08-0.10 (0.06-<0.19)	2.00±0.79 (1.07-2.90)
Demersal fish	0.05-0.09 (0.05-0.15)	1.11±2.16 (0.21-6.00)
Non-molluscan invertebrate	0.01-0.13 (<0.06-<0.22)	1.18±0.96 (0.11-2.40)
Mollusc	0.03-0.11 (<0.08-0.15)	81.60±105.72 (2.71-283.54)
Hoki	0.09 (0.05-0.13)	1.29±0.58 (0.77-1.91)
Arrow squid	0.00-0.16 (<0.12-<0.19)	1.95±0.54 (1.33-2.30)
All samples	0.05-0.12 (0.05-<0.22)	15.57±50.22 (0.05-283.54)

Detections of ^{137}Cs in the three tuna and one shark sampled were consistent with the results from lemonfish and tuna sampled in the radionuclide dietary survey in Chapter Two. The higher trophic level of these species likely facilitated bioaccumulation of ^{137}Cs. Similar results have been reported in other surveys of fish. For example, in a study of fish from Oman ^{137}Cs activity was recorded in the predatory pelagic species, such as albacore tuna (0.5 Bq/kg), bluefish (0.18-0.43 Bq/kg) and barracuda (0.25 Bq/kg) (Goddard et al., 2003). However a study of ^{137}Cs activities in fish caught off the south coast of India did not identify any statistically significant trends in terms of the feeding habits of the fish type sampled (Feroz Khan & Godwin Wesley, 2012).

All samples of oceanic pelagic species had detectable activity concentrations of ^{137}Cs with the exception of orange roughy (*Hoplostethus atlanticus*). Orange roughy is a migratory pelagic fish. However it tends to inhabit very deep water, congregating around submerged seamounts, a behaviour which differs from that of the other oceanic pelagic species sampled (Clark, 1999). Concentration factors for mesopelagic species are not considered to differ from those of surface species (IAEA, 2004). The most likely explanation for the lack of detectable ^{137}Cs in this species is the reported decrease in seawater activity concentrations of this isotope in deeper waters of the South Pacific Ocean (Ayoama et al., 2011).

There is no evidence that transfer of ^{137}Cs from Fukushima-Daiichi contaminated water has occurred for the migratory pelagic species with ranges extending to New Zealand. This is further confirmed through the comparable activities that were measured in non-migratory species, such as hoki and tarakihi, and the absence of ^{134}Cs activity concentrations (Table 4.2).

Residual oceanic contamination from historical nuclear testing is the most probable source for the ^{137}Cs activity concentrations detected in the seafood samples. Extrapolating from ^{137}Cs oceanic activity concentrations prior to the Fukushima-Daiichi accident allows the likely contribution from this source to be determined. The activity concentrations of ^{137}Cs in 2000 in the oceanic regions surrounding New Zealand were 0.6-1.4 Bq/m^3 (Povinec et al., 2004). A further study in 2003-4 undertook analysis for ^{137}Cs in surface waters on a longitudinal crossing of the South Pacific (30-32.5^{o}S), passing through the Tasman Sea and to the North of New Zealand (154-150^{o}E) (Hirose et al., 2007). ^{137}Cs activity concentrations in this transect ranged from 1.2-1.7 Bq/m^3. Decay adjusted to 2015 expected ^{137}Cs activity concentrations would therefore range between 0.45-1.4 Bq/m^3 or approximately 0.44- 1.4 mBq/kg seawater. Concentration factors of 100,

50, 60 and 9 have been published for the transfer of ^{137}Cs from seawater to finfish, crustaceans, molluscs and cephalopods respectively (IAEA, 2004). Considering this, expected ^{137}Cs activity concentration ranges for these species based on legacy global fallout would be: 0.045-0.14 Bq/kg for finfish, 0.026-0.07 Bq/kg for crustaceans, 0.027-0.084 Bq/kg for molluscs and 0.004-0.013 Bq/kg for cephalopods. These ranges encompass the majority of the detected activity concentrations for ^{137}Cs found in the tested New Zealand seafood. The absence of detectable activity concentrations for ^{137}Cs in the sampled arrow squid is also supported by the low concentration factors for cephalopods. The lack of activity concentrations in squid may also be a factor of the reported rapid depuration of radiocaesium by cephalopods. A study examining cuttlefish exposed to ^{134}Cs through the diet gave biological half-lives of 16 days for adults and 66 days for juveniles. For juveniles exposed to ^{134}Cs through seawater, depuration was much faster at an average biological half-life of 6 days (Bustamante et al., 2006).

It is therefore highly likely that the primary source of ^{137}Cs in the New Zealand marine region is from legacy nuclear fallout, particularly as ^{137}Cs activity concentrations are present and consistent in species from the more remote Sub Antarctic Islands fishery region. The consistency of the detected activities with the expected concentrations ranges from the historical fallout inventory supports this.

As activity concentrations of ^{137}Cs in New Zealand resident species were at or below the level of analytical determination, the full ranges for the coastal pelagic and demersal species have not been fully elucidated. This larger proportion of left censored data precluded statistical analysis of the results for species or regional variation, however regional variation of ^{137}Cs activity concentrations in resident finfish species around New Zealand appears low. The results from this chapter along with the results

presented in Chapter Two indicate that ^{137}Cs activity concentrations are within the ranges expected from the oceanic inventory of ^{137}Cs from global nuclear fallout.

Modelling of the future elevation of ^{137}Cs in the Pacific Ocean from the dispersion of the oceanic inventory released in the Fukushima-Daiichi accident, has estimated an elevation of up to 0.03 Bq/m^3 could occur in New Zealand coastal waters (Nakano & Povinec, 2012). By using the concentration factors for ^{137}Cs in various seafood groups this would result in an estimated increase of between 0.3 and 3 mBq/kg for species resident to New Zealand waters (IAEA, 2004). Based on the calculated seafood MDC of the gamma-spectroscopy protocol used in this study of 57-220 mBq/kg, such an increase is unlikely to be resolvable from the current activity concentration ranges occurring from global nuclear fallout.

4.3.2. Polonium-210 analysis

Calculated ^{210}Po recoveries ranged from 41 to 89% with a mean recovery of 71%. The mean percentage deviation between duplicates was estimated over five duplicate samples and one quadruplicate sample to determine the reproducibility of result. The mean percentage deviation between duplicates was 20%. This relatively high value was likely a consequence of the heterogeneous nature of ^{210}Po in shellfish replicates, which likely stemmed from ^{210}Po being bound to retained particulates which were not evenly distributed during sample processing. By removing the three shellfish duplicates the mean percentage deviation was reduced to 10%.

Detected activity concentrations, with associated standard error at 95% confidence, and assay MDCs for ^{210}Po are reported in Table 4.2. Higher MDCs were recorded in squid samples in comparison to the rest of the samples due to the one year time period between reported catch date and analysis, a factor that increased the analytical uncertainty. For the

remaining samples analysis was undertaken 1-2 months after catch date thus providing an accurate estimate of ^{210}Po in the freshly caught sample. A total of 92% of the 36 samples analysed contained ^{210}Po activity concentrations above the MDC, with the remaining samples reporting trace activity concentrations below the MDC. Samples with trace activity concentrations included a shark species. This was not unexpected as the activity concentrations in lemonfish (rig shark) reported in Chapter Two would have fallen below the MDC of this method (mean: 0.044 Bq/kg ww).

The activity concentrations of ^{210}Po in species within the same ecological niches were generally consistent (Table 4.3.). Statistical analysis indicated no significant differences ($p > 0.05$) between all fish groups (oceanic pelagic, costal pelagic and demersal) and non-molluscan invertebrates. However, the mollusc population was significantly elevated in ^{210}Po activity concentrations relative to oceanic pelagic fish (Mann-Whitney *U* test, Z = -2.322, N = 12, $p = 0.02$), coastal pelagic fish (Z = 2.374, N = 11, $p = 0.018$), demersal fish (Z = -2.786, N = 13, $p = 0.005$) and non-molluscan invertebrates (Z = -2.8, N = 12, $p = 0.005$).

In Chapter Two ^{210}Po activity concentrations were highest in shellfish species. This finding was confirmed in the current chapter, however the magnitude of the accumulation, and the variability between individuals, was much greater than previously shown, with accumulation varying by more than two orders of magnitude (Table 4.2). This variation is consistent with that reported overseas for shellfish (Table 4.4) and may relate to several factors such as species, season and region. For example, diverse species of molluscs have been reported to have differing susceptibility to accumulate ^{210}Po. Among molluscs collected in the intertidal zone of a region of the Portuguese coast of the North Atlantic, activities ranged from 5.8 Bq/kg for common cockle (*Cerastoderma edule*) to 283 Bq/kg in common periwinkle (*Littorina littorea*) (Carvalho, 2011).

A comparable range is visible in the New Zealand results with paua reported at 2.7 Bq/kg and queen scallops with an activity concentration of 283.5 Bq/kg.

Seasonal variation in the activity concentrations of ^{210}Po is common. The ^{210}Po activity in Mediterranean mussels (*Mytilus galloprovincialis*) increased four-fold from summer to winter (Aközcan & Uğur Görgün, 2013). The increase was correlated to the increased rainfall during autumn and winter with the source being increased land runoff of ^{210}Po. Another study examining temporal variation in ^{210}Po indicated that activity increased as a result of phytoplankton blooms (Wildgust et al., 1998), whereby increased scavenging of soluble ^{210}Po occurred due to the higher organic matter content in the water, with subsequent increased uptake by marine organisms. Activity is also expected to increase following spawning as body weight is lost causing a relative increase in concentrations in the soft tissue of the mollusc (Wildgust et al., 1998). Addressing seasonal variation in commercial seafood species is difficult due to the limited harvesting times of many of the species. The seafood samples in this survey were primarily obtained in the first half of the year from January to June. Consequently, based on the limited data, no trend can be analysed in the results to indicate if seasonal variation is significant.

The species analysed in the present study contained ^{210}Po activities that were generally consistent throughout the different fishing regions. This included tarakihi caught as the coastal pelagic species from all of the coastal regions, and the benthic herbivorous species of rock lobster and kina. Intra-species variation between squid and hoki samples was also low. If the shellfish activity concentrations are excluded from the results, the mean seafood activity concentration of ^{210}Po is 2.4 Bq/kg with a standard deviation of 5.9 Bq/kg. For the largely sedentary or non-

migratory species of fish and invertebrates the low regional variation is evidenced by the mean activity concentrations of these groups being 1.5 Bq/kg with a standard deviation of 1.3 Bq/kg.

No statistically significant differences ($p \geq 0.05$) were noted in ^{210}Po activity concentrations between any of the different regions. Overseas, regional differences in activities have been recorded. A comparison of Mediterranean mussels from two regions of the Turkish coast of the Aegean Sea showed a difference in ^{210}Po activity of 5 to 40 times between the sites (Aközcan & Uğur Görgün, 2013). The higher activities in one site were considered to result from the discharge of a river system giving an influx of ^{210}Po from land runoff into the area. Regions containing industries that release NORM can also influence ^{210}Po in molluscs. Water in the vicinity of a coal powered power plant in Malaysia was noted by the authors as having higher ^{210}Po activity than other locations around the coast (Alam & Mohamed, 2011).

In the current study the highest recorded ^{210}Po value was measured in queen scallops obtained from remote fishery areas in deeper waters off the Otago Peninsula. Influence from land based sources to this fishery is unlikely. Higher accumulation than in molluscs residing at shallower depths may be due to sediment contact or higher mobilisation of ocean-deposited ^{210}Pb into the deeper water. The gamma spectra for this sample showed gamma emission activity consistent with other ^{238}U decay nuclides, such as thorium-234(^{234}Th), bismuth-214 (^{214}Bi) and lead-214 (^{214}Pb), which would indicate that some degree of contribution of radionuclides from the surrounding sediment is occurring.

Table 4.4. Variation in ^{210}Po activity concentrations reported in studies of shellfish overseas compared with New Zealand harvested shellfish.

Country of origin	Species sampled (Binominal name)	^{210}Po activity concentration range (Bq/kg ww)	Reference
New Zealand	Bluff oyster (*Tiostrea chilensis*), Greenshell mussel (*Perna canaliculus*), Littleneck clam (*Austrovenus stutchburyi*), Paua (*Haliotis iris*), Queen scallop (*Zygochlamys delicatula*)	2.7-283.5	This chapter
New Zealand	Greenshell mussel (*Perna canaliculus*), Littleneck clam(*Austrovenus stutchburyi*), Pacific oyster (*Crassostrea gigas*)	20.8-29.4	Chapter Two
Croatia	Mediterranean mussel (*Mytilus galloprovincialis*)	22.1-207.0	Rozmaric et al., 2012
Kuwait	Clams (*Marica marmorata*, *Circe intermedia*, *Marcia opima*), Cockle (*Fulvia fragile*), Sea snail (*Stomatella auricular*, *Cerithium scabridum*)	2.7-53.3	Uddin & Bebhehani, 2014
India	Periwinkle (*Cerithium scabridum*)	13.5-58.9	Sunith Shine et al., 2013
India	Mussel (*Perna indica* & *Perna viridis*)	31.0-212.0	Feroz Khan et al., 2014
Slovenia	European flat oyster (*Ostrea edulis*), Mediterranean mussel (*Mytilus galloprovincialis*)	51.2-124.6	Štrok & Smodiš, 2011
Taiwan	Oyster (*Crassostrea gigas*)	23.4-126.0	Lee & Wang, 2013
UK	Blue mussel *(Mytilus edulis)*, Common cockle (*Cerastoderma edule*), Common limpet (*Patella vulgata*), Common periwinkle (*Littorina littorea*), Whelk (*Buccinidae* spp.)	2.9-52.1	Young et al., 2002

The most likely source of the ^{210}Po activities in the shellfish sampled in the current study is through their diet. This can be confirmed by using the activities ratio of ^{210}Pb and ^{210}Po to derive the contribution from the parent radionuclides in the uranium decay series. As both ^{210}Po and its grandparent ^{210}Pb are present in the marine environment, accumulation of ^{210}Po in seafood species can derive either from direct accumulation of the radionuclide (unsupported ^{210}Po) or through accumulation of ^{210}Pb and its subsequent decay to ^{210}Po *in situ* (supported ^{210}Po). ^{210}Pb activity can be quantified from its gamma emission at 46 keV. However, as the gamma emission has a low decay intensity (5%) the method sensitivity is poor, resulting in a higher MDC. As a consequence, in this study only two shellfish samples had detectable ^{210}Pb activity concentrations. Comparison of the ^{210}Pb activity concentrations with those of the ^{210}Po in the two shellfish samples with reported ^{210}Pb activity concentrations gives an estimation of the supported ^{210}Po. The comparison of ^{210}Pb:^{210}Po ratio determined 97-98% of the ^{210}Po activity concentration was unsupported. The low percentage of ^{210}Po present from decay of grandparent ^{210}Pb indicates that the primary source is direct uptake of ^{210}Po from the environment. ^{210}Po is particle reactive in the marine environment and readily binds to organic matter. The binding of ^{210}Po to organic matter results in concentration factors as high as 30000 into zooplankton and 70000 into phytoplankton (IAEA, 2004), and thus the consumption of these primary consumers is likely to be the source of ^{210}Po in species higher up the food chain.

A single high activity concentration of ^{210}Po, 32.77 Bq/kg, was noted in a skipjack tuna (*Katsuwonus pelamis*) sample. This was considerably higher than the other species of tuna (albacore and southern bluefin) and the other recognised oceanic pelagic species analysed. Tuna data from other studies indicate that muscle ^{210}Po levels can vary considerably,

ranging from 1.7 Bq/kg ww in the Eastern Pacific to 137 Bq/kg in the Mediterranean (Heyraud & Cherry, 1979; Ruelas-Inzunza et al., 2012). Yellowfin tuna from the south coast of India had a mean activity concentration of 19.9 Bq/kg (Feroz Khan & Godwin Wesley, 2012). What is notable about this latter study is that the activities of ^{210}Po reported in pelagic planktivorous species (e.g. anchovy, shad and sardine) were the highest of the finfish species sampled. Reported ^{210}Po activities in the pelagic planktivores ranged from 32.5 Bq/kg to 46.8 Bq/kg. The noted variation in ^{210}Po activity concentrations between tuna species and in comparison to planktivores supports the hypothesis that ^{210}Po activities reflect the diet of the species. As soluble ^{210}Po is scavenged to organic matter particulates, such as the small bacteria and algae present in plankton (Carvalho, 2011), planktivorous species take up more ^{210}Po than other species. Consequently the preference for consuming these species in an animal from a higher trophic level would influence the ^{210}Po uptake and retention in the tissues of the consumer.

4.3.3. Dose assessment for high seafood consumers

Seafood represents a significant source of nutrition for much of the population in New Zealand (University of Otago & MOH, 2011). The consumption of seafood in the diet, in combination with the higher natural levels of ^{210}Po present, likely makes it a high contributor to total dietary ionising radiation. Some sub-populations in New Zealand can be much higher consumers of seafood than the population average. These will include those populations where fish consumption is culturally important, those undertaking a large proportion of recreational fishing and seafood collection, and those relying on fishing and shellfish collection for sustenance due to economic reasons (Tipa et al., 2010; Turner et al., 2005). In the latest New Zealand adult nutrition survey, conducted in 2008, the mean consumption values for molluscs were 29 g/day, however

consumers at the 97.5th percentile ingested 240 g/day (University of Otago & MOH, 2011). This sub-population is potentially exposed to higher levels of ionising radiation due to the presence of foods with greater natural radionuclide activity concentrations.

To estimate the ranges of exposure a high seafood consumer may be receiving from natural and anthropogenic sources through their diet, a high consumption model was developed. Data from the seafood assays (Table 4.2.) was used to assign likely activities for both ^{210}Po and ^{137}Cs occurring in the diets of a high seafood consumer over the course of a year. The model was run both semi-probabilistically, through the use of set weekly consumption values, and fully probabilistically, through assigning a random weekly dietary consumption for each seafood type of between 0 and 1 kg. Estimates at a range of percentiles for ingested dose due to ^{137}Cs and ^{210}Po in seafood were obtained from the high consumer model (Table 4.5.).

Table 4.5. Probabilistic and semi-probabilistic exposure estimates for high seafood consumers of the annual committed dose through recorded activity concentrations of ^{137}Cs and ^{210}Po in New Zealand seafood.

Probabilistic Model	**Radionuclide**	**High seafood consumer dietary radionuclide exposure at *n*th percentile (µSv/person/year)**					
		5th	**25th**	**50th**	**75th**	**95th**	**99th**
Semi	^{137}Cs	0.046	0.047	0.048	0.049	0.051	0.052
Full	^{137}Cs	0.11	0.12	0.12	0.12	0.13	0.14
Semi	^{210}Po	443	520	576	635	721	784
Full	^{210}Po	1874	2312	2652	3028	3605	4047

The results of the dietary modelling show the current ^{137}Cs activity concentrations in seafood represent a minimal contribution to the total dose for high seafood consumers. This exposure differs little with the

types of seafood species consumed over a year with a negligible difference in dose between the 5th and 95th percentiles. When compared to the reference dose level of 1 mSv/yr, adopted for dietary risk characterisation in Section 3.2.2., ^{137}Cs in New Zealand seafood currently represents a negligible concern (ICRP, 2007).

In comparison, the dose from natural ^{210}Po exposure is approximately 10000 times higher, ranging up to a 99th percentile exposure of 0.78 mSv/yr in the semi-probabilistic model and 4.05 mSv/yr in the probabilistic model. In comparison to the semi-probabilistic dietary doses calculated in Chapter Three for adults, the semi-probabilistic doses for high seafood consumer adults from ^{210}Po are between five to ten fold higher. The ^{210}Po dose varied considerably depending on the composition of seafood making up the diet, with the range between the 5th and 95th percentiles encompassing 0.28 mSv (0.44-0.72 mSv) in the fixed consumption and 1.7 mSv (1.87-3.61 mSv) in the random consumption models. This range was expected given the large variation in the activities between different species of each seafood group. Individual consumers with a large intake of shellfish, in particular scallops and oysters, are likely to receive the highest dietary doses of radionuclides across the New Zealand population. As established in Section 4.3.2 the ^{210}Po source in New Zealand fisheries is most likely of natural origin. The extent of dose from ^{210}Po in a seafood diet is therefore considered part of the range of background doses received within a population and falls outside current guidelines on regulating ionising radiation exposure (ICRP, 2007). However the extent of the contribution from ^{210}Po to a seafood dietary dose highlights that enhancement of background activities with releases from an anthropogenic source would potentially lead to significant dietary burden. As was reported in the example of Whitehaven in Section 1.2.5

this could lead to a considerable dose which may exceed the adopted reference dose level of 1 mSv.

The large contribution of ^{210}Po activity concentrations in seafood to dietary doses has been reported for a range of other countries, including India and Lebanon. (Feroz Khan & Godwin Wesley, 2011; Aoun et al., 2015). In a further study in India, average consumption of values of 25 kg/yr for each seafood type were determined to lead to annual committed doses of 0.59 mSv, 0.61 mSv and 3.36 mSv from ^{210}Po in marine finfish, prawns, and crabs, respectively (Kannan et al., 2001). In this later study despite seafood species accounting for only 3% of the composition of the Indian diet model they accounted for 81% percent of the dietary dose of ^{210}Po.

The dose from ingestion of ^{210}Po is part of the variation in natural background radiation between diets. Of interest is an estimate of the dose prehistoric coastal dwellers of South Africa, the Khosian, received from a characterised high shellfish diet (Heyraud et al., 1994). Based on modern day monitoring of shellfish from the Cape of Good Hope it was calculated that the Khosian would have received an annual dose of 4 mSv as a result of ^{210}Po. This dose is comparable to the maximum obtained in the full probabilistic modelling for New Zealand high seafood consumers and suggests that doses of this magnitude are ubiquitous for seafood consuming populations.

4.4. Conclusion

This study of activities of ^{137}Cs and ^{210}Po in New Zealand seafood has determined their respective current activity concentration ranges. ^{137}Cs activity was present predominantly in finfish, but all detected activity concentrations were very low and occurred in a small range above and below the MDC. No apparent variation was present between regions which is consistent with the source of ^{137}Cs being the diffuse residue from historical nuclear weapons fallout. No evidence of contribution to ^{137}Cs

activities from the Fukushima-Daiichi nuclear accident has been noted in either migratory or non-migratory species. Based on published modelling it is unlikely that any elevation in ^{137}Cs in New Zealand resident seafood species could be measured using the current analytical methods.

^{210}Po was present in the majority of seafood samples. Activities for molluscs showed a large range from 2 to 283 Bq/kg and this group of seafood biota was significantly elevated over the other seafood groupings. Ranges of ^{210}Po activity concentrations for other seafood species tended to be less diverse. No significant regional variation was recorded. Analysis of ^{210}Pb in two mollusc samples suggests that the ^{210}Po present is primarily accumulated through the diet.

Dose estimates for high seafood consumers based on the derived activities indicate that current activities of ^{137}Cs represent a minimal dietary concern. ^{210}Po activities, however, can contribute significantly to the dietary dose of ionising radiation for high seafood consumers, although the magnitude varies considerably depending on the composition of seafood species consumed. Due to the activities of ^{210}Po, the high seafood consuming sub-population is likely to receive the highest dietary ionising radiation doses for the New Zealand population.

Chapter 5 – Activity concentration ranges of radium-226 and radium-228 in New Zealand agricultural soils, and inputs from phosphate fertilisers

5.1. Introduction

Enhanced levels of NORM pose potential long-term risks to public health (IAEA, 2003). As outlined in Chapter Four, New Zealand has no domestic nuclear industry and is geographically isolated from nuclear sources overseas. Anthropogenic sources of radionuclide contamination are therefore less of a risk than in many other nations. However, contamination with NORM can occur outside of the nuclear industry, particularly in mineral extraction and utilisation, a process referred to as TeNORM (IAEA, 2013b). For New Zealand TeNORM presents a more probable long-term scenario for increasing exposure to ionising radiation than other anthropogenic sources. To forecast future radiological risks to the New Zealand population, the influence of TeNORM and routes through which it can enter the New Zealand food supply, require investigation.

Phosphate fertiliser manufacturing is an industry at risk of producing enhanced levels of NORM in a range of fertiliser products and by-products (García-Talavera et al., 2011; IAEA, 2013b). Due to low natural levels of phosphate in its soils, the New Zealand agriculture industry is dependent on phosphate fertilisers to maintain soil fertility (McLaren & Cameron, 1996). However, phosphate ores can contain a number of elemental contaminants, of which several are implicated in impaired human health (Gupta et al., 2014; MAF, 2011; Sabiha-Javied et al., 2009). To date, with the exception of research on accumulation of uranium (Taylor, 2007; Schipper et al., 2011), the potential implications of NORM as a contaminant in phosphate fertilisers in New Zealand have not been addressed.

Internationally, the focus on NORM in relation to phosphate products relates to the potential for concentration of uranium. The concentration of uranium occurs due to the manufacturing process used to refine phosphate rock into the feedstock phosphoric acid for triple super-phosphate (TSP), or other refined phosphate products such as di-ammonium phosphate (DAP) and nitrogen, phosphate and potassium (N.P.K.) complexes (IAEA, 2013b). While concentrating uranium, the manufacturing process for phosphoric acid tends to precipitate the decay series daughters into the waste phosphogypsum, and as such these are less of a consideration for the final fertiliser product. Phosphogypsum presents a number of radiological risks, predominately with the storage of waste stacks (Al Attar, 2011). However, with the exception of a few countries, phosphogypsum usage is limited in an agricultural context.

New Zealand differs from many agricultural nations in that the most common form of phosphate fertiliser is single superphosphate (SSP). In the manufacturing process of SSP there is no elution step, and so no loss of the decay series radionuclides from the final product occurs (Packer et al., 1998). Another type of fertiliser with a small market share in New Zealand, reactive phosphate rock (RPR), generally undergoes no chemical processing, so similarly has no net loss of decay radionuclides. The lack of uranium concentration that occurs in these products and the retention of daughter nuclides in the uranium and thorium decay series offers a very distinct radiological risk profile for phosphate fertiliser application in New Zealand. However, very little is known regarding the extent of this risk, especially with respect to the daughter nuclides that are largely excluded from phosphate applications internationally.

Of the radionuclides present in the uranium and thorium decay series, ^{226}Ra is of particular concern. This nuclide has a high potential for substantial dietary exposure through agricultural and horticultural

products. This is based on its moderate level of decay, which facilitates soil accumulation, and thus results in a high potential for uptake into crops. For example, the relative uptake rate of ^{226}Ra is greater than that for lead, uranium, polonium and thorium (IAEA, 2010). ^{226}Ra may also accumulate to levels in top soils greater than those predicted from the secular equilibrium of its grandparent, ^{238}U (Greeman, 1999). Finally, as a result of a moderate gastrointestinal absorption rate and long term persistence in the body, both ^{226}Ra and ^{228}Ra have high dose coefficients (ICRP, 2012).

The last comprehensive studies of ^{226}Ra activity in New Zealand soils were undertaken in the 1970s (Baltakmens, 1976; Dobbs & Matthews, 1976). As such, little research on environmental levels of radium has been undertaken in the last 40 years. Consequently, there is no useful baseline for establishing what the impacts of fertiliser sources may be on the radium levels in soils. This chapter addresses this data gap by establishing the activity concentrations of ^{226}Ra and ^{228}Ra in a range of New Zealand soils. In addition, by using sequential extraction methods, this work establishes the partitioning of ^{226}Ra into the different soil fractions, data that are critical for determining how available radium may be for crop uptake.

5.2. Materials and methods

5.2.1. Phosphate rock and fertiliser sampling

To identify the range of radium inputs into New Zealand soils, 18 phosphate products were obtained for analysis of ^{226}Ra and ^{228}Ra. It is common practice in New Zealand for different rock sources to be blended in the manufacture of SSP, and as such activity concentrations in the fertiliser may differ depending on the blend. To obtain the likely ranges of activity concentrations, nine phosphate rocks of different geological origins that are, or have historically been, used in fertiliser manufacture

were sampled (Ores 1-9). Additionally, single batch samples of commercially-available single SSP and TSP fertilisers were analysed (SSP and TSP respectively). Finally, a small number of other fertiliser products were analysed, including three RPR samples (RPRs 1-3), three DAP samples (DAPs 1-3) and a single sample of a N.P.K. complex fertiliser (Complex). Due to the commercial sensitivity of the manufacturing process, the origin of the ores and blend ratios or other chemical properties are unable to be presented.

5.2.2. Soil samples

A wide range of agricultural top soils were obtained from across New Zealand to characterise the activity concentration ranges of ^{226}Ra and ^{228}Ra. From duplicate plots of 19 horticultural and pastoral growing sites, 15 cm soil cores were sampled in 2015. Additionally, a separate set of thirteen 15 cm soil cores sampled in the years between 2008-14, from sites in the Waikato (n = 8) and Greater Wellington (n = 5) regions of New Zealand were obtained. These encompassed a range of land uses and soil orders. Locations of the sampling sites by region are presented in Figure 5.1. (Cavanagh, J., personal communication 01 August 2016).

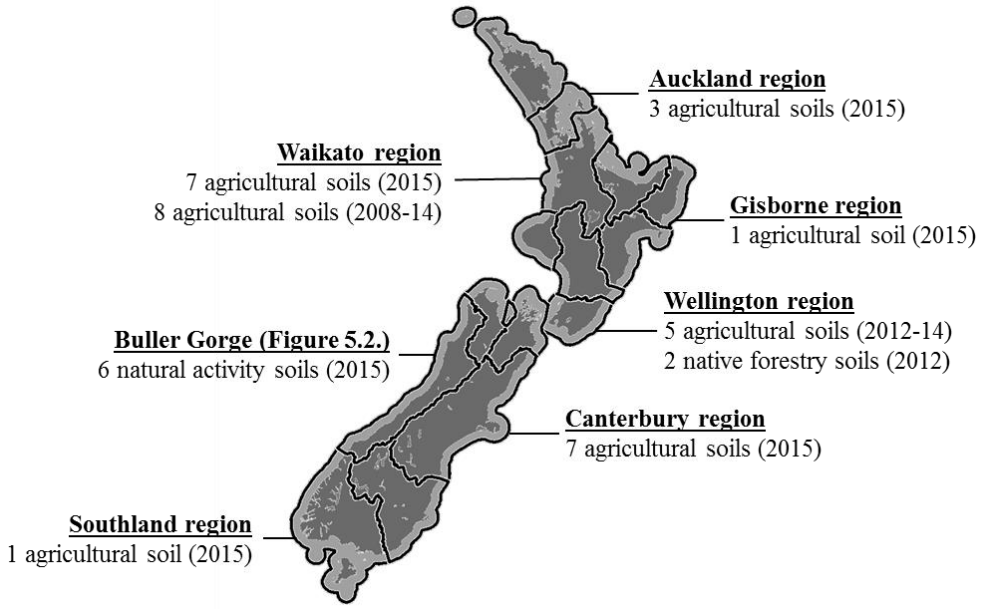
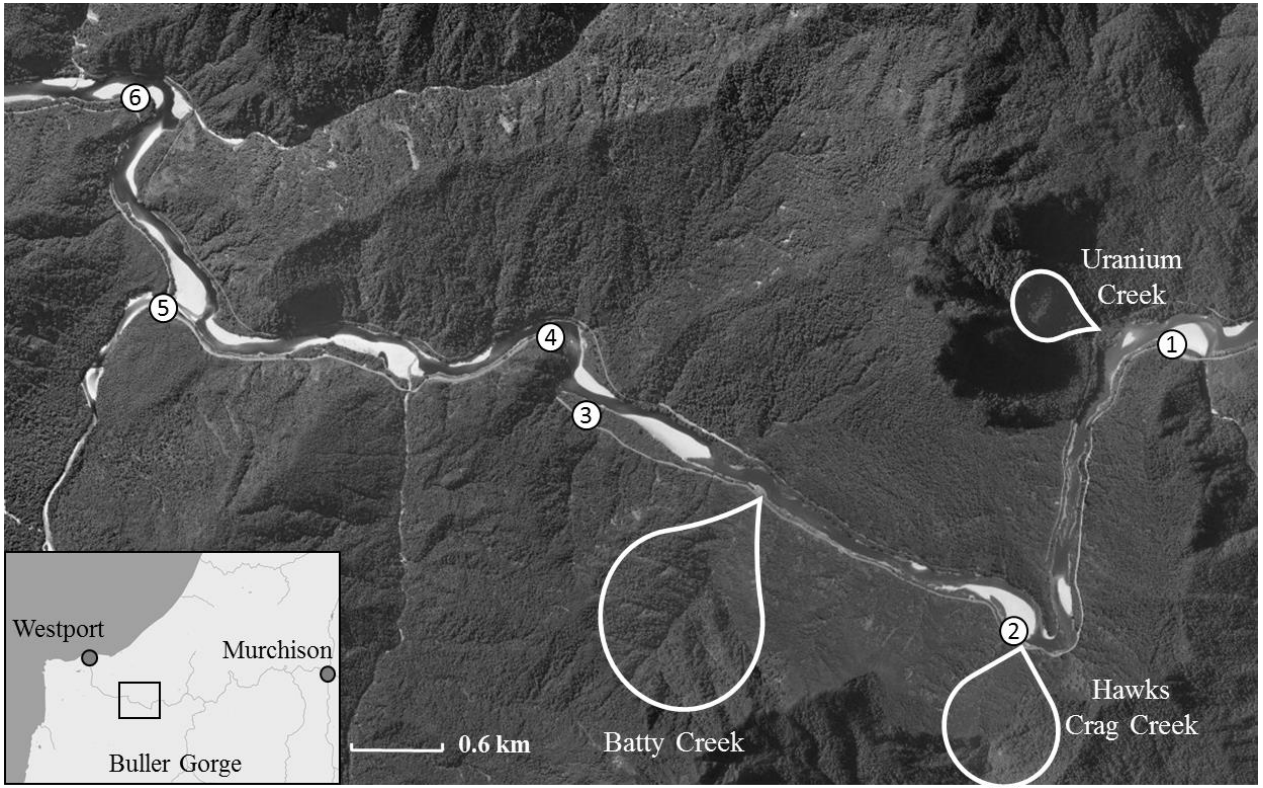


Figure 5.1. Soils sampling sites by regions of New Zealand for analysis for ^{226}Ra.

Source: Adapted from Landcare Research, 2016.

To provide natural comparisons two samples from native forestry sites in the Greater Wellington region with no reported chemical inputs, were obtained. Additionally, six soil cores (0-15 cm) were sampled in triplicate from an area reported to contain bedded uranium deposits to allow a comparison to soils with naturally elevated activity. Samples were taken from a section of the Buller Gorge, the lower section of the Buller River following from Murchison to the outflow into the Tasman Sea at Westport (Figure 5.2.).



Sampling site coordinates:

1: 41°50'50.8"S, 171°47'25.5"E;

2: 41°51'42.1"S, 171°46'31.5"E;

3: 41°51'04.7"S, 171°44'38.6"E

4: 41°50'49.1"S, 171°44'32.5"E;

5: 41°50'42.7"S, 171°42'44.5"E;

6: 41°50'01.2"S, 171°42'18.6"E.

Figure 5.2. Soil sampling sites in an area of reported high background activity in the Buller Gorge, West Coast region. Drainage basins into the Buller River from areas reported to contain bedded uraniferous deposits are highlighted.

Sources: Inset adapted from Landcare Research, 2016a; Data based on Beck et al., 1958; Wodzicki, 1959.

5.2.3. Soil fractionation

Detailed analysis was undertaken to identify the geochemical partitioning of ^{226}Ra in New Zealand topsoil fractions and determine if this correlated to soil properties. The thirteen soil samples from the Waikato and Greater Wellington regions were used for this analysis. The soil origins and properties of the selected soils are presented in Table 5.1. Excluding the two native soils, the targeted soils were of high fertility, measured through Olsen P, as a potential marker for inputs of phosphate fertilisers. Additionally cadmium values for these soils were recorded. Whilst cadmium is not believed to interact with radium behaviour it is an important contaminant resulting from phosphate fertilisers so can also be used as a marker of fertiliser input to soils (MAF, 2011). Two Buller Gorge soil samples from Site 1 (recorded as Sample 16) and Site 4 (recorded as Sample 17; Figure 5.2.), classified as podzol soils, and which exhibited the highest ^{226}Ra activity concentrations, were also analysed.

A sequential extraction method was undertaken at the Massey University Institute of Agriculture and Environment to separate ^{226}Ra activity present in the each of the labile fractions (Schultz et al., 1998). The labile fractions were: the easily soluble and ion exchangeable fraction (termed the exchangeable fraction); the fraction sorbed to soil organic matter; the fraction bound to soil carbonates; and the fraction that was bound to soil iron and manganese oxides and oxyhydroxides. Activity of ^{226}Ra in the non-labile fraction, that which remains tightly bound to the soil silicate structural complexes, was also measured in the residual material.

Table 5.1. Soil origins, orders and chemical properties for samples undergoing sequential extraction of fractions.

Sample number	Region	Land Use	Soil Order	Olsen P (mg/kg)	pH	Carbon (%)	Exchangeable cations ($cmol^{(+)}/kg$)				Cadmium (mg/kg)
							Ca	Mg	K	Na	
1	Waikato	Dairy	Allophanic	66	6.2	10.04	20.1	3.51	1.45	0.32	1.80
2	Waikato	Dairy	Pumice	250	6.6	9.33	25.6	3.27	1.42	0.21	0.48
3	Waikato	Horticulture	Granular	122	6.8	6.42	16.8	1.33	0.67	0.35	1.00
4	Waikato	Dairy	Allophanic	286	4.9	9.11	22.0	4.24	3.08	0.23	0.58
5	Waikato	Beef	Allophanic	287	5.3	10.71	7.1	1.81	1.60	0.12	0.90
6	Waikato	Dairy	Pumice	354	6.7	10.9	14.1	2.18	2.59	0.8	1.70
7	Waikato	Horticulture	Allophanic	82	5.4	11.88	37.2	5.36	1.69	0.17	0.19
8	Waikato	Dairy	Pumice	260	5.4	9.37	12.7	1.53	1.83	0.31	0.66
9	Wellington	Beef	Brown	161	6.8	5.1	12.5	2.73	1.89	0.26	0.43
10	Wellington	Dairy	Pallic	102	6.5	6.8	21.9	4.26	1.23	0.54	0.63
11	Wellington	Horticulture	Recent	196	6.4	1.4	12.0	0.91	1.42	0.07	0.39
12	Wellington	Horticulture	Gley	159	5.9	4.81	15.7	1.82	1.40	0.18	0.19
13	Wellington	Horticulture	Brown	184	7.3	1.32	16.1	1.96	0.84	0.13	0.20
14	Wellington	Native forestry	Pallic	9	7.1	6.8	19.8	3.09	0.53	0.33	0.12
15	Wellington	Native forestry	Brown	10	5.5	13.1	23.2	5.62	1.23	0.39	0.07
16	West Coast	River bank	Podzol	Data not collected							
17	West Coast	River bank	Podzol	Data not collected							

Sources: Drewry, 2013a; Drewry, 2013b; Drewry, 2014; Drewry, J., personal communication 05 May 2015; Taylor. M, personal communication 04 March 2016.

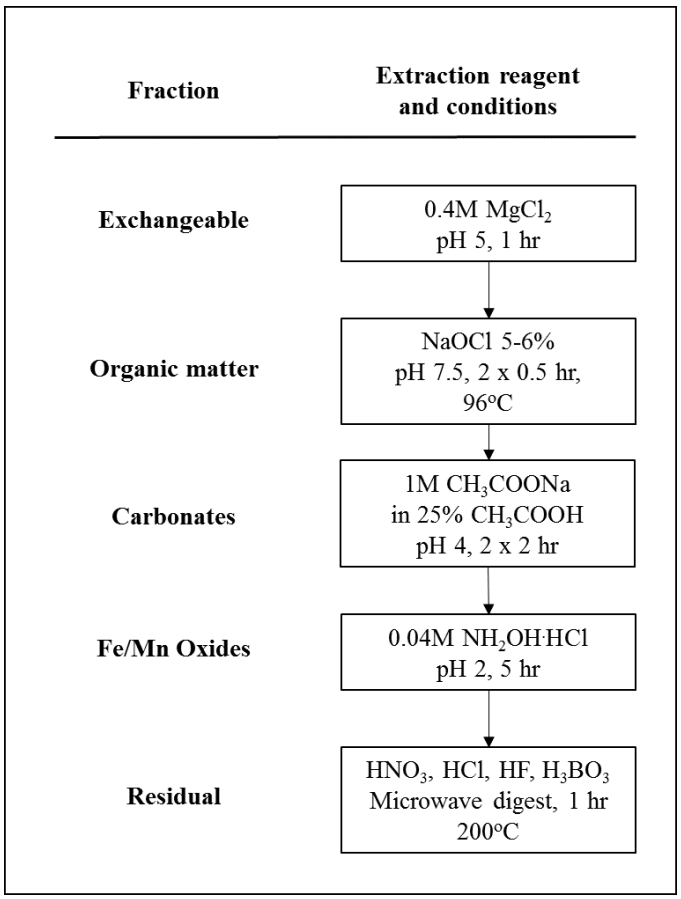


Figure 5.3. Sequential extraction procedure for fractionation analysis of ^{226}Ra in soil.

Source: Schultz et al., 1998.

Approximately 2 g dw samples of each soil were fractionated using a modified sequential extraction method for actinides reported by Schultz et al. (1998) (Figure 5.3.). This method has been tested for reproducibility on ^{226}Ra fractionation by Blanco et al. (2005). Prior to undertaking the extraction process, samples were wetted overnight in 2 ml water to rehydrate incorporated clays. Extraction of each of the fractions was then undertaken consecutively over the course of two days. All fraction reagents in Figure 5.3. were added to samples at a ratio of 15:1. For the exchangeable and oxide fractions the reagent was added to the sample all

at once. For the organic matter and carbonate fractions, following the directions of the procedure developed by Schultz and colleagues (1998), the reagent addition was split evenly between the commencement of the extraction with the remaining amount added halfway through the stage. During the extraction the samples were kept agitated in a custom-built sample tumbler at room temperature for the stated period. An exception was for the organic matter extraction, where samples were maintained in a water bath at 96°C to facilitate the digestion of organic material. Following each extraction stage the samples were centrifuged for 18 minutes at 9000 x *g* and extraction reagents then decanted. Reagent blanks for each extraction were also analysed. A subsample of 0.2 g of the residual solid phase was digested in a microwave digester using a mixture of 8 ml analytical grade HNO_3 (70%; Fisher Scientific), 5 ml analytical grade HCl (37%; Fisher Scientific), 1 ml HF (47%; Ballance) and 5 ml H_3BO_3 (5%). The temperature was increased up to 200°C over 15 minutes and then maintained for 1 hour. Two of the soils were analysed in duplicate to determine the variability in the method.

5.2.4. Analysis of radium

Radium analysis was undertaken using standard protocols for alpha spectrometry and gamma spectroscopy (IAEA, 2010a). ^{228}Ra has very low gamma emission probabilities and the characteristic gamma emission for ^{226}Ra (186 keV) suffers interference from the 186 keV emission of ^{235}U (IAEA, 2014). Direct quantification of both isotopes by gamma spectroscopy is therefore difficult in environmental samples. Gamma spectroscopy quantification of ^{226}Ra and ^{228}Ra is reliant on establishing secular equilibrium with short-lived progeny with strong gamma emissions (^{214}Pb and ^{214}Bi for ^{226}Ra (Appendix A, Figure A.4.) and actinium-228 (^{228}Ac) for ^{228}Ra; IAEA, 2014). As ^{226}Ra initially decays to gaseous radon-222 (^{222}Rn), the samples need to be hermetically sealed to prevent

atmospheric loss of ^{222}Rn. For alpha spectrometry ^{226}Ra can be chemically separated and measured directly by its 4.6 MeV alpha emissions without interference from other radium or daughter isotopes.

All bulk soil samples were oven dried at 80 °C, ground and homogenised. Phosphate ore and fertiliser samples were provided pre-ground. Approximately 60 g subsamples of each phosphate ore or fertiliser, and 6 g samples of each soil, were mixed with an epoxy resin and hermetically-sealed within an appropriate sized plastic petri container. Sample mass was adjusted for any loss during mixing. After a 30 day in-growth period, samples were analysed in a Canberra HPGe gamma spectrometer. ^{226}Ra was indirectly counted through the gamma emissions from ^{214}Pb and ^{214}Bi based on secular equilibrium being maintained. ^{228} Ra was indirectly counted through the gamma emissions of ^{228}Ac based on secular equilibrium being maintained.

A sequential lead and barium co-precipitation method was used on 10 ml samples of the soil fraction extracts to separate ^{226}Ra. Samples were made up to 500 ml in water adjusted to pH 1 with 0.1M HCl, and a barium-133 (^{133}Ba) yield tracer was added. With gentle heating and stirring, 2 g K_2SO_4 was dissolved in the solution, and 3 ml H_2SO_4 was added, followed by addition of 0.24 M $Pb(NO_3)_2$ until $PbSO_4$ precipitated. The suspension was centrifuged, decanted and the precipitate washed with 0.1 M H_2SO_4. The precipitate was then dissolved in 10 ml of warm 0.2 M EDTA at pH 10 before 4 ml saturated Na_2SO_4 solution and 10 ml water was added. A 1 ml carrier solution of 50 μg Ba^{2+}(as $BaCl_2$) and 0.1 ml $BaSO_4$ seeding solution were added, followed by adjustment of the solution to pH 4.5 with 1 M acetic acid. The solution was mixed and refluxed for 30 minutes at 60 °C then the precipitate filtered out using a 25 mm, 0.1 μm Resolve filter. The filter was mounted and analysed for 1 hour by gamma spectroscopy to determine tracer yield, and by alpha spectrometry for 23 hours to quantify

^{226}Ra alpha emissions at 4.6 MeV. To establish method recovery a one-hour count was undertaken in each gamma detector of a filter directly spiked with a gravimetrically recorded mass of the ^{133}Ba tracer. Reference filter counts were repeated each week to ensure the reference activity remained accurate. The percentage method recovery was then calculated through comparison of the tracer yield in each sample against that of the reference filter in the utilised gamma detector, results are presented as recovery corrected. A 15% bias was deducted from the final result to account for the different geometry of the sample filters to the spiked filter.

5.2.5. Data analysis

Quality assurance of the radioanalytical methods was provided through the laboratory's participation in proficiency test exercises organised by the IAEA and the UK National Physical Laboratory (IAEA, 2013a; Dean et al. 2014). Quality control counts were undertaken monthly for the Alpha Spectrometer, with background counts generated as required. For the gamma spectroscopy quality control checks were undertaken monthly on each instrument and three day background measurements conducted every 6 months. Additional quality assurance steps included matrix spikes to validate methods for the alpha spectrometry, and confirming the method accuracy with IAEA proficiency samples.

Results for all samples are reported as Bq/kg dw. Minimum Detectable Concentrations (MDCs) were calculated for each assay according to the method defined by Currie (1968).

Statistical analysis was undertaken on untransformed data using the Pearson's Correlation coefficient and R values generated. Significance of R values was calculated in Microsoft Excel 2010 using the Student T-test and n-2 degrees of freedom. To account for the introduction of Type I error with undertaking a large number of pairwise analyses, false discovery rate

control was undertaken. False discovery rate control is designed to set a threshold in the rate of errors in significant results which are true null hypothesis (Benjamini & Hochberg, 1995). The obtained *p* values are sorted in ascending order. Each individual value is divided by the number of independent tests with the result multiplied by the false discovery rate. Descending through the results where the value is no longer greater than or equal to the corresponding *p* value this level is set as the threshold and all results following are deemed non-significant. The false discovery rate control has been applied to the statistical analysis of the derived *p* values in this study, using a false discovery rate of 0.1. This provides confidence that no more than 10% of the results deemed significant are false positives.

5.3. Results and discussion

5.3.1. Phosphate ore and fertilisers

Activity concentrations of ^{226}Ra were detected in all of the phosphate ore samples, ranging from 107 – 1649 Bq/kg, with an average of 662 Bq/kg (Figure 5.4.). ^{228}Ra, however, was detected in only six of the ores, ranging between 7.7- 486 Bq/kg with an average of 96 Bq/kg. Only one ore sample had ^{228}Ra in excess of ^{226}Ra, at a ratio of 0.2 ^{226}Ra:^{228}Ra. For all of the other samples analysed the activity concentration of ^{226}Ra exceeded ^{228}Ra with ratios ranging from 11-146 ^{226}Ra:^{228}Ra. The high ^{226}Ra:^{228}Ra is consistent with reports of natural radioactivity in most sedimentary phosphate sources reported internationally (IAEA, 2013b; Hassan et al., 2016). Generally, levels of ^{232}Th decay series nuclides only exceed 100 Bq/kg in igneous sources of phosphate (da Conceição & Bonotto, 2006; IAEA, 2013b; Saueia et al., 2013).

Consistent with the activity concentrations reported in the ores, the three RPR samples tested had considerable ^{226}Ra (419 - 1608 Bq/kg) and low ^{228}Ra (11 - 43 Bq/kg) activity concentrations. These products undergo

no processing except for milling, so a consistent profile to the phosphate ore was expected.

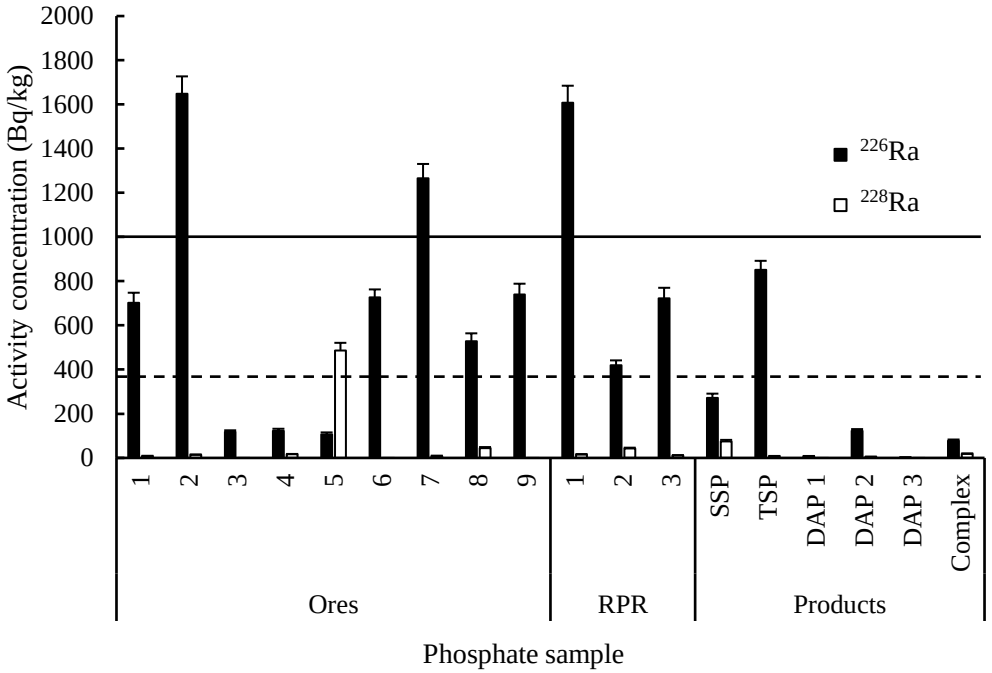


Figure 5.4. ^{226}Ra and ^{228}Ra activity concentrations in imported phosphate ores, reactive phosphate rocks (RPR) and fertiliser products used in New Zealand. US (dashed line) and Brazilian (solid line) regulatory limits for ^{226}Ra activity in phosphogypsum are identified (US EPA, 1998; CNEN, 2011).

The analysis of the manufactured fertilisers indicated appreciable ^{226}Ra activity concentrations only in the SSP (272 Bq/kg), the TSP (851 Bq/kg) and DAP sample 2 (123 Bq/kg). The other two DAP samples and the N.P.K. complex had low ^{226}Ra at a range of 2.5-77 Bq/kg. The presence of significant ^{226}Ra in the TSP sample and the DAP sample was unexpected as ^{226}Ra is predominately eluted into the waste phosphogypsum during the feedstock phosphoric acid production of these fertilisers (IAEA, 2013). Examining the gamma spectra for both products indicates that both have

high activity concentrations for ^{234}Th and ^{234m}Pa (2.4-2.8 kBq/kg; Appendix A, Figure A.5.). This indicates that even with some degree of concentration of ^{238}U during manufacture, the feedstock ore activity was likely very high and thus ^{226}Ra remains high despite a proportion being eluted during manufacture. No limits are placed on ^{226}Ra activity in superphosphate fertiliser to be applied to agricultural land, however for phosphogypsum the US has established a limit of 370 Bq/kg and in Brazil a limit of 1 kBq/kg is in place (CNEN, 2011; US EPA, 1998). The three RPR samples and the TSP sample would exceed the former guideline, while the Brazilian limit would be exceeded by only one of the RPR samples.

The activity concentration of ^{228}Ra was low for all the fertiliser products, however the activity reported in the SSP (75 Bq/kg) exceeded that present in the majority of the phosphate ores. In the production of SSP a range of ores from different geographical origins are usually blended to ensure a consistent final product. Blending may also be undertaken to ensure cadmium levels meet nationally agreed limits (FANZ, 2015). The activity concentration of ^{228}Ra in the SSP suggests the presence of a higher ^{232}Th rock, such as phosphate ore Sample 4, in the blend. The significance of blending is that the radium activity concentrations in the SSP can vary depending on the origin of the ore. This would result in differing loadings of radium to agricultural soils over time depending on the availability of certain ore types. Overall, the range of ^{226}Ra in the phosphate ores and its presence in the most heavily used product types suggests it can present a potential source of input to New Zealand soils. Conversely, ^{228}Ra, and by extrapolation ^{232}Th, is less significant and thus fertilisers are less likely to be a significant input of these nuclides to New Zealand soils.

5.3.2. Background and levels in naturally-elevated soils

Activity concentrations were measured for ^{226}Ra and ^{228}Ra in the six Buller Gorge soils and the two native forestry soils (Table 5.2.). Both native forestry soils had similar ^{226}Ra activity concentrations at 26.7 ± 3.3 and 28.6 ± 6.2 Bq/kg. ^{228}Ra activity concentrations were similar at 27.4 ± 5.1 and 26 ± 4.3 Bq/kg. Mean native forestry activity concentrations were 27.7 ± 4.7 Bq/kg ^{226}Ra and 26.7 ± 4.7 Bq/kg ^{228}Ra.

The ^{226}Ra activity concentrations in the Buller Gorge samples encompassed a very wide range of 34.7 ± 4.3 to 80.5 ± 7.1 Bq/kg, with a mean of 56.2 ± 5.5 Bq/kg. The Buller Gorge has been historically reported to contain deposits of the uranium bearing ore coffinite $(U(SiO_4)_{1-x}(OH)_{4x}$; Beck et al., 1958). The ^{226}Ra in these ores would be expected to be in secular equilibrium with the ^{238}U given the age of the geology in the region. Erosion and leaching from exposed rock would therefore contribute to elevated activity concentrations of ^{226}Ra in the local soils. The variation in ^{226}Ra activities at each of the sites represents the localised areas of reported coffinite lodes in the Buller Gorge (Beck et al., 1958; Wodzicki, 1959). Site 3 displayed the highest ^{226}Ra, which is consistent with it being the first sampling site downstream from the reported coffinite lodes around Batty Creek (Figure 5.2; Beck et al., 1958). Previous work with sediments on the west coast of New Zealand had identified ranges of ^{226}Ra between 7-22 Bq/kg (Marx et al., 2005), so all of the Buller Gorge samples in the current study show elevated concentrations relative to previous measurements.

Table 5.2. Radium activity concentrations in background soils and soils from the uraniferous area of the Buller Gorge.

Sampling site	^{226}Ra activity concentration ± uncertainty (Bq/kg dw)	^{228}Ra activity concentration ± uncertainty (Bq/kg dw)
Native forestry site 1	26.77 ± 3.32	27.42 ± 5.14
Native forestry site 2	28.62 ± 6.18	25.95 ± 5.14
Buller Gorge site 1	67.56 ± 6.09	72.15 ± 8.74
Buller Gorge site 2	47.77 ± 5.17	63.05 ± 8.93
Buller Gorge site 3	80.51 ± 7.07	57.77 ± 7.86
Buller Gorge site 4	34.74 ± 4.25	47.79 ± 7.55
Buller Gorge site 5	52.14 ± 5.03	44.14 ± 6.58
Buller Gorge site 6	54.39 ± 5.59	47.87 ± 8.12

The ^{228}Ra range in the collected samples was 44.1 ± 6.6 to 72.2 ± 8.7 Bq/kg with a decreasing gradient being notable along the seawards course of the river. This value compares well to ^{232}Th concentration data from seven dust and sediment samples from the closely located West Coast glaciers, which showed levels of 7.9 – 15 ppm (equivalent to 31.6-60 Bq/kg ^{232}Th; Marx et al., 2005). It is therefore likely that the ^{228}Ra activity concentrations in the soils in the Buller Gorge reflect the background activity in the region. In contrast the ^{226}Ra is elevated over the background for the region as a result of the localised sources of ^{238}U bearing coffinite ore in the region. The soils from the Buller Gorge can therefore be considered naturally elevated in activity for ^{226}Ra and are a useful contrast to soils where radionuclide accumulation may be from anthropogenic activity.

5.3.3. Ranges of radium in agricultural soils

All of the New Zealand agricultural soils analysed had detected activity concentrations of ^{226}Ra, within a range of 26 ± 2 – 88 ± 8 Bq/kg and a

mean of 46 ± 5 Bq/kg (Table 5.3). Most of the soils lay close to the mean, with the 5 - 95th percentile range being 34 ± 3 - 70 ± 7 Bq/kg ^{226}Ra. The reported activities fit within the reported range in the literature for uranium in New Zealand soils. Analysis of 1043 soils (0-10 cm) of various non-background land uses from across New Zealand gave a uranium concentration range of 0.01- 9.54 ppm (McDowell et al, 2013). Assuming secular equilibrium is maintained, this equates to a range of 0.1- 115 Bq/kg ^{226}Ra. However, the mean uranium concentration reported of 1.48 ppm (equivalent to 18 Bq/kg ^{226}Ra) is considerably lower than that found in the present study. This is reasoned to be the result of the inclusion of non-agricultural soils, such as from urban areas and forestry plantations, in the previous analysis. There may be other factors involved though, as a recent geochemical monitoring survey of soil samples (0-30 cm) from 348 sites in the lower South Island of New Zealand reported a maximum uranium concentration of only 2.5 ppm (equivalent to 31 Bq/kg ^{226}Ra), with a median of 0.7 ppm (equivalent to 9 Bq/kg; Martin et al., 2016). This represents a considerably lower range than the soils taken in the present study suggesting there may be some discrepancy in the reported uranium concentrations to the activity concentrations derived for ^{226}Ra in the present study. An important factor is likely to be that as the acid digestion protocol used by Martin and colleagues did not utilise HF, complete recovery of the uranium from the soils may not have occurred. Another potential explanation is this results from differences in the chemical behaviour of uranium to radium in the top-soils, with greater loss of the former from the top-soil over-time. Notably, the range and median for uranium in the Martin et al. study (2016) remained consistent in the samples of the deeper 30-60 cm soil horizons. Additionally, the result for ^{226}Ra in the present study established activity concentrations in the Southland region were at the lower end of the range for the agricultural

soils, indicating that spatial variability between regions could be an important consideration.

The last comprehensive monitoring of ^{226}Ra in New Zealand soils was in the 1970s with three studies being published from that time period. In the first analysis, four soil cores from different regions provided ^{226}Ra activity concentrations and their variation with soil depth. The topsoil (0-20 cm) activity concentrations ranged from approximately 20 Bq/kg to 30 Bq/kg (Baltakmens, 1974). A second study analysed 320 soil samples, of unspecified land use, covering the length of the country. The reported range of ^{226}Ra activity concentrations was <4 – 56 Bq/kg with an average of 23 Bq/kg. In that study, the activities were characterised by soil type, with peat soils having a significantly lower mean activity concentration of ~4 Bq/kg and Greywacke- and Loess-derived soils having the highest mean activity concentration of 26 -29 Bq/kg (Dobbs & Matthews, 1976). Finally, a separate study of 210 soil cores (0-20 cm) derived ranges for ^{226}Ra activity concentrations for soils of basaltic origin, igneous origin and sedimentary origin. The ranges were 4 – 41 Bq/kg with a mean of 21 Bq/kg for basaltic; 9 - 33 Bq/kg with a mean of 20 Bq/kg for igneous; and 4 – 37 Bq/kg with a mean of 18 Bq/kg for sedimentary origin soils (Baltakmens, 1976). All three studies signify that soil activity concentrations have increased in the intervening four decades to reach the values reported in the present study.

Table 5.3. Radium activity concentrations in agricultural soils from different regions of New Zealand.

Region	Land Use	^{226}Ra activity concentration ± u (Bq/kg dw)	^{228}Ra activity concentration ± u (Bq/kg dw)
Auckland	Horticulture	72.48 ± 5.69	77.84 ± 7.14
Auckland	Horticulture	88.26 ± 7.58	102.07 ± 10.95
Auckland	Horticulture	67.07 ± 6.52	77.23 ± 9.05
Canterbury	Arable	49.71 ± 4.95	56.81 ± 7.82
Canterbury	Arable	44.95 ± 4.64	47.16 ± 7.37
Canterbury	Arable	43.89 ± 4.76	45.72 ± 6.34
Canterbury	Horticulture	42.37 ± 4.33	44.32 ± 5.93
Canterbury	Horticulture	50.06 ± 4.33	53.60 ± 5.84
Canterbury	Pasture	43.28 ± 4.04	39.99 ± 5.55
Canterbury	Pasture	43.50 ± 3.95	41.65 ± 5.30
Gisborne	Horticulture	38.67 ± 4.33	42.34 ± 6.11
Southland	Arable	29.96 ± 3.44	21.08 ± 5.05
Waikato	Arable	34.97 ± 3.81	32.10 ± 5.36
Waikato	Horticulture	43.43 ± 4.63	44.29 ± 6.33
Waikato	Horticulture	39.10 ± 4.62	40.82 ± 6.54
Waikato	Horticulture	61.73 ± 8.23	43.37 ± 7.13
Waikato	Horticulture	44.42 ± 4.96	26.34 ± 5.20
Waikato	Pasture	35.27 ± 3.50	34.47 ± 5.45
Waikato	Pasture	38.89 ± 3.98	33.10 ± 5.32
Waikato	Pasture	38.09 ± 3.63	35.66 ± 6.20
Waikato	Pasture	36.01 ± 4.38	33.20 ± 5.86
Waikato	Pasture	56.76 ± 5.59	38.30 ± 6.63
Waikato	Pasture	34.75 ± 3.86	28.15 ± 6.26
Waikato	Pasture	38.29 ± 4.26	37.79 ± 6.72
Waikato	Pasture	64.51 ± 6.05	69.04 ± 8.98
Waikato	Pasture	33.44 ± 3.56	34.12 ± 5.68
Waikato	Pasture	39.38 ± 3.96	35.22 ± 6.17
Wellington	Horticulture	55.79 ± 4.77	58.96 ± 5.53
Wellington	Horticulture	55.71 ± 4.70	67.29 ± 5.88
Wellington	Horticulture	25.55 ± 2.43	27.01 ± 3.49
Wellington	Pasture	35.66 ± 4.59	37.57 ± 5.92
Wellington	Pasture	33.54 ± 3.61	36.01 ± 5.62

In the present analysis, all of the agricultural soils analysed had quantified activity concentrations of ^{228}Ra. Activity concentrations for ^{228}Ra ranged between 21 ± 5 – 102 ± 11 Bq/kg with a mean of 45 ± 6 Bq/kg. The 5-95th percentile range for ^{228}Ra was equivalent to that of ^{226}Ra at 28 ± 5 – 78 ± 9 Bq/kg. No data regarding ^{228}Ra in New Zealand soils have been previously reported. However, assuming secular equilibrium is maintained with ^{232}Th the soils monitored in the Dobbs & Matthews (1976) study would have had an average ^{228}Ra activity concentration of 29 Bq/kg with a range of <4 to 62 Bq/kg. The study of 210 soil cores also reported ^{232}Th activity concentrations amongst the soil classes, with mean activities for ^{232}Th of 23 Bq/kg for sedimentary origin and 25 Bq/kg for basaltic and igneous origin soils (Baltakmens, 1976). ^{226}Ra and ^{228}Ra activity concentrations in the agricultural soils analysed are therefore elevated over natural background sites, and against the results of historical monitoring undertaken in the 1970s. In the case of both radium isotopes the increase in the mean is approximately two-fold, with the highest reported values for ^{226}Ra also being double that of the historical monitoring. As these soils are all from fertile agricultural land phosphate fertiliser has to be considered the primary input for this elevation. However, it is identified that there are other explanations for the observed increase. For example, tilling of the soils could have resulted in lower soil strata with higher activities being brought to the surface. The Martin et al. (2016) geochemistry study noted that the median concentration of thorium was greater in soils of 30-60 cm depth (1.45 ppm; equivalent to 6 Bq/kg ^{228}Ra) than in the top 30 cm (0.9 ppm; equivalent to 4 Bq/kg ^{228}Ra). This explanation is unlikely for all the soils however, and would be unlikely to lead to the increase in soil activity concentrations recorded.

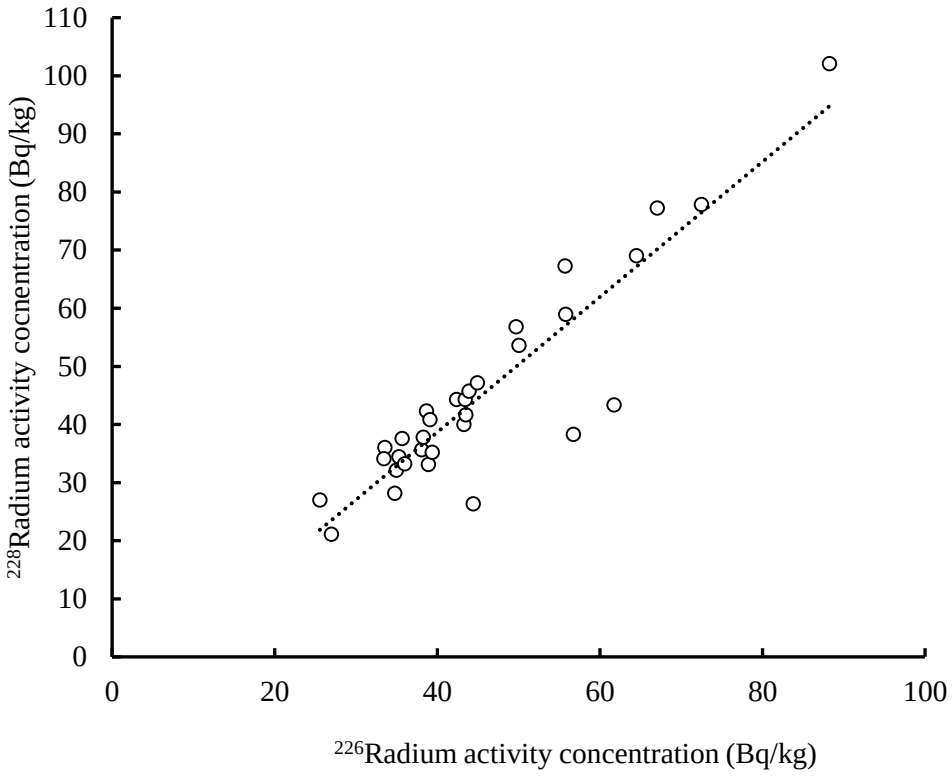


Figure 5.5. Relationship between the measured activity concentration values for ^{226}Ra and ^{228}Ra in thirty-two New Zealand agricultural soils. Typical uncertainties are 5 Bq/kg for ^{226}Ra and 6 Bq/kg for ^{228}Ra.

There is a marked linear correlation between ^{226}Ra and ^{228}Ra activity concentrations across all of the New Zealand agricultural soils (R^2 = 0.8325 p = <0.0001; Figure 5.5.), at a mean ratio of 0.98±0.24 ^{228}Ra:^{226}Ra. This replicates the reported results from the study of 310 soils undertaken in the 1970s where a strong linear relationship was seen with most of the soil types between ^{226}Ra and ^{232}Th. While the mean ^{232}Th:^{226}Ra ratio in that study, of 1.2, is larger than that of ^{228}Ra:^{226}Ra in the current work the change is not considered significant given the uncertainties (Dobbs & Matthews, 1976). In the previous study, the correlation between the two radium nuclides was considered to relate to the ratios of both elements in the minerals from which the soils were formed. As phosphate fertilisers

contain elevated activity concentrations of ^{226}Ra and are largely deficient in ^{228}Ra. As a result a gradual change over time in the ratio between both isotopes in soil could be expected from the use of phosphate fertilisers. This is expanded on in Section 5.3.5.

5.3.4. Soil fractionation

Seventeen soils, including two native sites and two sites from a uraniferous area were analysed by sequential extraction. Measured activity concentrations in each of the obtained fractions was calculated as a percentage of the sum of activity from all of the fractions. Recovery in all fractions, compared to bulk activity in the soils, was an average of 67%. For all of the soils the majority (>90%) of the ^{226}Ra remained bound in the residual fraction (range 91.8% to 98.3%; Figure 5.6.). ^{226}Ra activity in the labile soil fractions was generally consistent amongst the range of soils (Figure 5.7.). Only the organic matter fraction showed a wide range of activity, with between 0.77% and 6.05% of the total activity being present in this fraction. Intra-day reproducibility indicated a mean of 29% variation across the fractions between duplicates. Analysis of the variation indicates it was largely driven by differences in the oxide fraction, and may be more dominated by counting statistics as the activities are close to the assay minimum detectable concentration.

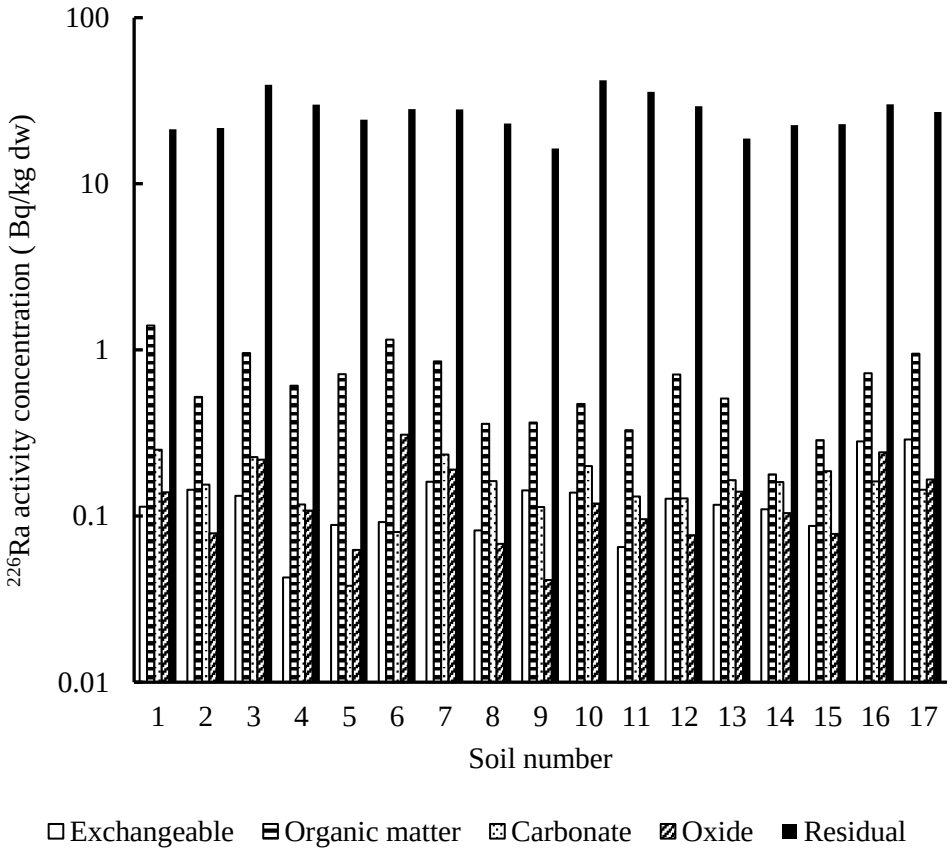


Figure 5.6. ^{226}Ra activity concentrations determined in the different fractions following sequential extraction analysis of the 17 New Zealand soils detailed in Table 5.1.

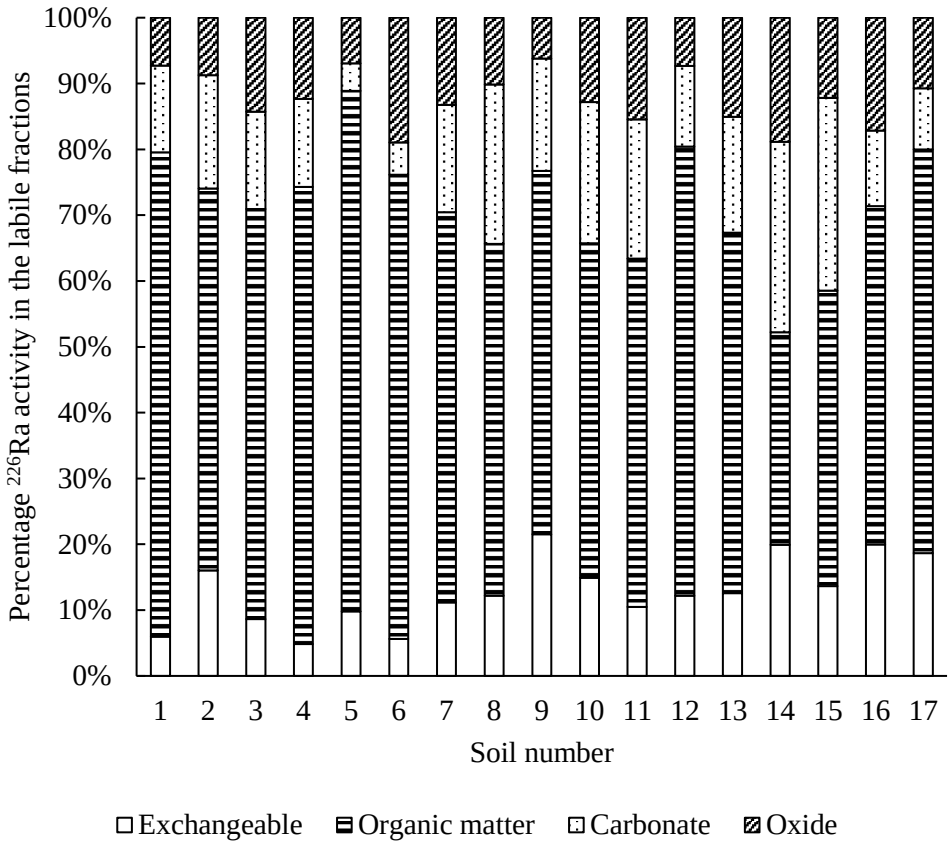


Figure 5.7. Percentage ^{226}Ra activity concentrations determined in the labile fractions following sequential extraction analysis of the 17 New Zealand soils detailed in Table 5.1.

The ^{226}Ra fractionation profiles for the New Zealand soils analysed are common with most uncontaminated soils in that the majority of ^{226}Ra remains bound in the residual fraction and very little is available in the oxide fraction. However, the low proportions of ^{226}Ra activity concentrations in the exchangeable and carbonate fractions differs from the higher values of previous international studies. For example, a study of soils around a uranium mine tailing dump, reported that in the uncontaminated soil samples close to 80% of activity was in the residual phase, with about 8% each in the carbonate and organic matter fractions

(Štrok & Smodiš, 2010). A study of boreal forest soil samples was undertaken in Finland, with ^{226}Ra activity concentrations of approximately 10-60 Bq/kg reported (Virtanen et al., 2013). While the largest proportion (average 57%) of ^{226}Ra was bound in the residual phase, significant levels were also present in the exchangeable fraction (an average of 17%), and the carbonate fraction (an average of 13%). In the analysis of two soils from Spain, approximately 50% of the ^{226}Ra was bound in the residual, 25% in the carbonate and 12% in the organic matter fractions. One of these soils was TeNORM-affected and the other unaffected by TeNORM, but the two soils showed similar fractionation profiles (Blanco et al., 2005). In the New Zealand soils in the current study a similar proportion of ^{226}Ra was reported in the exchangeable fraction as that reported in the Spanish soils. However, the percentage in the oxide fraction in the New Zealand soils was considerably higher.

Fractionation studies often differ with respect to both the sequence and reagents. Previous work has validated the current method for ^{226}Ra but some differences in the ^{226}Ra activity elution profile can be expected (Blanco et al., 2004). A noted concern with the Schultz method used in this chapter is that the reagent used in the organic matter fraction may dissolve some carbonates out of sequence (Schultz et al., 1998). Although this is a concern, it was not noted as a factor in the work of Blanco and colleagues (2004). Where a higher percentage of ^{226}Ra activity was eluted in the carbonate fraction than the organic matter fraction, with a robust coefficient of variation of 12%. Nonetheless, given the differences between fractionation studies it is likely that the analysis of relative differences between the soils analysed in this chapter will be of more value than comparison of absolute values against those of other studies.

There were insufficient native soils to allow robust statistical comparisons between the native and the agricultural soils. However, it is

notable from the two background activity sites that the proportion of ^{226}Ra bound in the organic matter fraction was at the lower end of the ranges. For the two naturally high activity sites in the Buller Gorge the proportion of ^{226}Ra in the exchangeable fractions was higher than any of the other soils analysed.

Correlation analysis was performed between radium activities and soil properties for all of the soils except samples 16 and 17, where properties were not available (Table 5.4.). With increasing total soil ^{226}Ra there was an associated significant increase in the measured activity in the organic matter fraction (R^2 = 0.733, p = 0.002), and a weaker correlation to increases in the oxide fraction. With increasing soil ^{226}Ra activity concentrations, relative increases in activity across all fractions would be expected. The correlations of the activity in fractions against the total activity suggests that ^{226}Ra added to soil is preferentially bound into the organic matter and potentially to the oxide fraction. Availability of radium in the exchangeable and carbonate fraction appears independent of the total activity in soil and is likely influenced by other soil chemical properties.

Correlation analyses showed a significant negative linear correlation between the Olsen P values and the ^{226}Ra activity concentration reported in the carbonate fraction (R^2 = 0.4979, p = 0.003). By limiting the data to only the agricultural soils, the correlation became stronger. The data showed a best fit to a log-linear relationship (R^2 = 0.7066, p = <0.001; Figure 5.8.).

Table 5.4. Correlation coefficients for multiple comparisons of ^{226}Ra activity concentrations and fractionation against soil chemical properties (n = 15).

Soil Property	Exchangeable fraction		Organic matter fraction		Carbonate fraction		Oxide fraction		Residual fraction		Bulk soil	
	^{226}Ra (Bq/kg)	^{226}Ra %	^{226}Ra (Bq/kg)	^{226}Ra %	^{226}Ra (Bq/kg)	^{226}Ra %	^{226}Ra (Bq/kg)	^{226}Ra %	^{226}Ra (Bq/kg)	^{226}Ra %	^{226}Ra (Bq/kg)	^{226}Ra/ ^{228}Ra
Olsen P (mg/kg)	-0.399	-0.249	0.169	0.137	**-0.706***†	**-0.629***	0.155	0.139	-0.009	-0.009	0.236	-0.322
C (%)	-0.037	-0.093	0.316	0.298	0.080	0.082	0.175	0.168	-0.145	-0.272	-0.009	0.455
pH	0.422	0.430	-0.055	-0.014	0.129	0.203	0.251	0.331	-0.050	-0.114	0.015	-0.208
Ca (cmol$^{(+)}$/kg)	0.432	0.166	0.093	0.041	**0.642***	0.483	0.205	0.200	0.076	-0.155	-0.147	**0.675***
Mg (cmol$^{(+)}$/kg)	0.186	0.121	-0.031	0.009	0.408	0.395	-0.023	0.023	-0.084	-0.084	-0.368	0.427
K (cmol$^{(+)}$/kg)	-0.458	-0.272	0.238	0.228	-0.448	-0.378	0.132	0.113	-0.048	-0.115	0.224	-0.062
Na (cmol$^{(+)}$/kg)	0.017	-0.169	0.294	0.155	0.028	-0.113	**0.605***	0.512	0.219	-0.163	0.236	-0.124
Cd (mg/kg)	-0.126	-0.198	**0.811***†	**0.758***†	-0.010	-0.082	**0.537***	0.489	0.101	**-0.658***	**0.627***	0.216
Total ^{226}Ra (Bq/kg)	-0.030	-0.338	**0.733***†	0.502	0.031	-0.279	**0.590***	0.369	0.448	-0.385	n/a	0.240

* p = <0.05; † Correlations remaining significant following Benjamini-Hochberg false discovery rate control (107 tests, false discovery rate of 0.1).

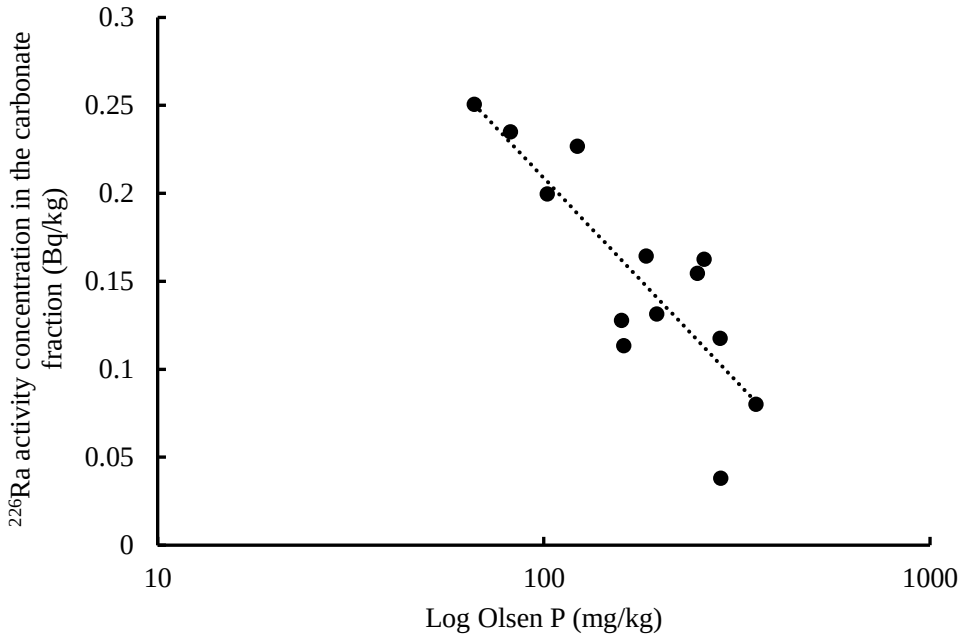


Figure 5.8. Relationship between the measured ^{226}Ra activity concentrations in the carbonate fraction of 13 agricultural soils and the soil Olsen P concentration.

There was a significant positive relationship between available calcium and the ^{226}Ra activity reported in the carbonate fraction (R^2 = 0.4119, p = 0.001). Exploring this trend further, there was a significant negative correlation between the Olsen P:Ca ratio for the bulk soil and the percentage of the activity present in the carbonate fraction across all of the soils (R^2 = 0.48, p = 0.004). This correlation remained significant following false discovery rate analysis. This is hypothesised to be a function of increased precipitation of calcium phosphates. As the ratio of calcium to available phosphate increases, co-precipitation of ^{226}Ra results. As calcium phosphates would be expected to dissolve in the weak acid of the carbonate fraction reagent (NaAc), any co-precipitating ^{226}Ra would also be recovered in this fraction (Von Wandruszka, 2006). Competition of Ra^{2+} with other soil cations for binding sites in soil fractions is well

reported (IAEA, 2014). However, with the range of soil types studied, and a large number of variables, no single factor is likely to be the critical determinant of binding of ^{226}Ra, and its subsequent availability to plant uptake. This is a conclusion also reached by Vandenhove and Van Hees (2007).

Olsen P is a measure of plant available phosphate, but it is not necessarily a direct measure of superphosphate inputs. Other agricultural inputs such as manures will contribute organic phosphate into the soil available phosphate (Laboski & Lamb, 2003). Because of this, cadmium may be an alternative proxy for long-term superphosphate inputs. This trace metal contaminant accumulates in the soil, largely owing to superphosphate addition (MAF, 2011). Total soil ^{226}Ra positively correlated with soil cadmium across the fifteen soils, although the correlation did not remain significant after false discovery rate control (Table 5.3.). This supports the hypothesis that increased radium is associated with increased fertiliser input. Cadmium concentration was strongly and positively correlated to the percentage of ^{226}Ra binding in the organic matter fraction (R^2 = 0.5753, p = 0.001) and negatively correlated to percentage binding in the residual phase. In US soils ^{226}Ra has been reported to be predominantly bound to the organic matter (Greeman et al., 1999). It is therefore hypothesised that superphosphate inputs of ^{226}Ra are preferentially sorbed to organic matter in the soil, increasing the relative binding to that fraction.

A number of other chemical factors could be important for binding in the residual phase. Barium will be of particular relevance in the SSP samples. Trace levels of barium have been found in some sedimentary phosphate ore sources, whereas barium may reach concentrations of up to 15 g/kg in igneous phosphate ore sources (da Conceição & Bonotto, 2006; Rentería-Villalobos et al., 2010;). In the da Conceição and Bonotto

(2006) study, barium was retained at similar levels into the SSP products but not detectable in the TSP or monoammonium phosphate products. Due to the use of sulphuric acid in SSP manufacture, a proportion of the barium could be expected to precipitate out as barite ($BaSO_4$), a process highly likely to co-precipitate radium (Benes & Strejc, 1986; Grandia et al., 2008; Rutherford et al., 1996; Santos et al., 2006). Barite is highly insoluble and will leach slowly in soil, particularly if sulphate levels remained high, as would be expected from the concurrent addition of gypsum ($CaSO_4$) in a SSP fertiliser (Huck et al., 1989). A study into barite fractionation reported that the precipitate may be extracted in the oxide fraction (Ippolito & Barbarick, 2006), suggesting co-precipitating ^{226}Ra would also elute into this fraction. Retention in the residual phase may also be a strong possibility. In a study of ^{226}Ra fractionation in Brazilian phosphogypsum, which also contained 11 g/kg of barium, >99% of the ^{226}Ra and Ba was retained into the residual fraction (Silva et al., 2002). If this was the case for New Zealand SSP it would explain the high percentages of ^{226}Ra reported in the residual fraction of the agricultural soils. Additionally it may explain the discrepancy in the soil concentrations of uranium reported in other geochemical studies to the ^{226}Ra activity concentration ranges in Section 5.3.3. for agricultural soils. Barite would be highly resistant to weathering and thus may retain the co-precipitated ^{226}Ra in top-soils whilst uranium leaches out over time.

The ratio of barium to cadmium in the phosphate ore would also provide an explanation for the significant correlation reported for cadmium against ^{226}Ra binding in the organic matter fraction. Some phosphate sources, for example the marine phosphate nodules on New Zealand's Chatham Rise, can be high in uranium and barium, but have very low cadmium levels (Cullen, 1980; EPA, 2015). Long-term use of fertiliser products manufactured from ores containing high barium concentrations

would lead to greater co-precipitation of ^{226}Ra and reduce its availability to bind to the labile phases. Whilst low cadmium concentrations would limit the long-term accumulation in the soils.

5.3.5. Historical trends in soil accumulation

As part of the 1976 study of 320 New Zealand soil samples, a forecast of accumulation of ^{226}Ra in soil as a result of phosphate fertiliser applications was made (Dobbs & Matthews, 1976). The authors calculated an annual increase of 0.085 Bq/kg ^{226}Ra in soil as a result of an annual fertiliser application of 350 kg/ha containing 370 Bq/kg ^{226}Ra. It is observed that over the 40 years between the Dobbs & Matthews study and the current study this would equate to an overall increase of 3.2 Bq/kg ^{226}Ra in soil. However, assuming the land uses of the soils in both studies are sufficiently comparable, the calculated increase in ^{226}Ra for agricultural soils in Section 5.3.3, would be nearly seven times greater than this, at approximately 0.58 Bq/kg a year. Notably, an annual loading estimate was also made for ^{232}Th of 4 mBq/kg, equating to an accumulation of only 0.16 Bq/kg over 40 years. Assuming secular equilibrium has been maintained, the activities of ^{228}Ra appear to have actually increased by two orders of magnitude from those predicted.

Annual application rates of phosphate fertilisers will not necessarily remain static over time, large “capital” applications can be made to bring soil fertility up to a desired level and then “maintenance” applications made annually to retain the fertility. Additionally different cropping situations will have different nutritional requirements so applications may vary. The annual fertiliser rate used in the Dobbs and Matthews (1976) study is within the typical annual application range for pastoral land of 200-600 kg SSP/ha but below the high rates of upto 1 tonne SSP/ha that may be used in potato production (Mills et al., as cited in MAF, 2008, p. 32). However, the extent of the difference noted in the measured ^{226}Ra

soil activity against that predicted would still not be fully accounted for even at the rates used for potatoes.

One explanation for the difference between predicted and measured ^{226}Ra loads is that the estimate of the amount of ^{226}Ra being loaded on to land (370 Bq/kg) was too conservative. The results in Section 5.3.1 show that the ^{226}Ra activity concentration can vary significantly, depending on the blend of ores used. In fact, current activity concentrations can reach five times those predicted in the Dobbs and Matthews study (1976). Similarly, other phosphate sources, such as RPR, can have similar higher-than-predicted activity concentrations. This is supported by a study of uranium accumulation in New Zealand pastoral soils (Schipper et al., 2011). In this study, at an annual application of fertiliser at 50 kg P/ha, the soil concentration increased from 1.07 ± 0.11 mg/kg uranium, assuming secular equilibrium equivalent to 13.2 ± 1.4 Bq/kg ^{226}Ra, to 1.28 ± 0.12 mg/kg uranium (15.8 ± 1.5 Bq/kg ^{226}Ra) after 5 years, and 2.03 ± 0.21 mg/kg uranium (25.1 ± 2.6 Bq/kg ^{226}Ra) after 23 years. This was calculated as an estimated annual rate of accumulation of 0.042 ± 0.015 mg/kg uranium (0.5 ± 0.2 Bq/kg ^{226}Ra), which is close to that estimated for ^{226}Ra above. However, in the Schipper et al. study (2011) it was reported that uranium loading to the soil was 10-fold greater than would have been expected, based on application of single superphosphate with up to 460 Bq/kg ^{238}U. Similarly, in an earlier study of four New Zealand soils the annual uranium accumulation rates were reported as ranging between 0.015-0.47 mg/kg (0.2-0.6 Bq/kg ^{226}Ra; Taylor, 2007), fitting closely with the increases reported in the current chapter.

The underestimate of loading may also apply to ^{228}Ra. In making their predictions, Dobbs & Matthews (1976) used a value of 18 Bq/kg for ^{232}Th. Assuming secular equilibrium, the ^{228}Ra present in the single superphosphate analysed in Section 5.3.1 was 75 Bq/kg, and based on the

ores it is feasible to reach application rates of this nuclide as high as 486 Bq/kg. Additionally while ^{228}Ra was not detected in Section 5.3.1 as a major contaminant in most of the phosphate products, it may be present in other nutrient supplements that are applied in significant concentrations to agricultural land, such as dolomite clays or lime. Taylor (2007) reported both types of product contained ^{238}U in the ranges of 26-56 Bq/kg. Monitoring results for ^{232}Th or ^{228}Ra activity concentrations have not been examined for these products in the current study.

5.4. Conclusion

Analysis of phosphate ores imported into New Zealand, and manufactured fertiliser products available on the New Zealand market, indicate a wide range of ^{226}Ra activities. Single superphosphate, triple superphosphate and reactive phosphate rocks all have significant activity of ^{226}Ra. Conversely, ^{228}Ra is low in most of the ores and products. Phosphate fertiliser as a source of ^{226}Ra to New Zealand agricultural land is supported by the analysis of 32 agricultural soils showing an elevation above background sites and soil monitoring values from the 1970s. Soil activity concentrations for ^{228}Ra have also increased, although the source of this is unknown. For both radium isotopes the increase is higher than that predicted by previous research.

Analysis of ^{226}Ra fractionation in soils indicates a range of factors are likely to influence its binding to soil constituents. ^{226}Ra activity correlates with cadmium concentration, indicating that input is through phosphate fertilisers, with this nuclide preferentially binding to the soil organic matter. Available calcium and phosphate influence binding in the carbonate fraction, with the hypothesis that co-precipitation of ^{226}Ra with calcium phosphates may be occurring in high calcium soils. With the exception of two natural elevated activity sites, ^{226}Ra does not preferentially remain in the exchangeable fraction.

Chapter 6 – Current and forecasted increases of radium-226 and radium-228 doses in the diet through uptake into crop plants

6.1. Introduction

The presence of ^{226}Ra as a contaminant in the phosphate fertilisers used in New Zealand creates the potential risk that any elevation in soil ^{226}Ra activity concentrations may be transferred to food and feed crops. Radium can readily accumulate in topsoil as it does not significantly leach to deeper soils. A review by Roessler (1988) estimated only a 2% loss of radium from the root zone annually. Additionally a study of radium mobility in pot trials irrigated with ^{226}Ra enriched ground water indicate minimal migration below 15 cm for a loamy-sandy soil and below 35 cm for a fine-sandy soil (Tripler et al., 2014). Chapter Five identified that ^{226}Ra activity concentrations have accumulated over time in New Zealand agricultural soils raising the question of what the current and future implications of the increase are for the ionizing radiation dose received by the New Zealand population. The dietary modelling in Chapter Three presented a comprehensive picture of doses for many radionuclides of both natural and anthropogenic origin. However, as ^{226}Ra and ^{228}Ra activity concentrations were not obtained for the New Zealand diet, UNSCEAR values were used to estimate likely exposures (UNSCEAR, 2000). With the range of activities for both isotopes now established in agricultural soils in Chapter Five there is the opportunity to estimate the activity concentrations, and therefore ionizing radiation dose, that may result in the New Zealand diet. Additionally with the estimates of annual loading rates for ^{226}Ra calculated in Section 5.3.5., it is possible to forecast how the dietary ionizing radiation dose will increase over time. The calculated increase in dose can be used to estimate when, or if, regulatory intervention and mitigation may be necessary.

Plant uptake of radionuclides can occur through two mechanisms (Vandenhove et al., 2009). The first is foliar uptake, whereby deposition of the radionuclide occurs on the plant surface and is absorbed into the plant. Foliar uptake is an important route for anthropogenic fallout radionuclides, but also ^{210}Pb and ^{210}Po due to the decay of atmospheric ^{222}Rn gas and subsequent wet or dry deposition of ^{210}Pb onto the plant surface (Al-Masri, 2010; Coppin & Roussel-Debet, 2004; Štrok & Smodiš, 2012). For ^{226}Ra this route is only likely to be of importance in the vicinity of atmospheric releases of NORM, for example burning coal, where fallout of the airborne particles on to plants occurs (Zeevaert et al., 2006). The second route of transfer to plants is root uptake from the soil. For ^{226}Ra root uptake is likely to be a far more significant mechanism of accumulation and is often used as a contrast to atmospheric fallout radionuclides (Sheppard et al., 2008).

The basic calculation for deriving the degree of plant accumulation of an element is to divide the plant concentration by that present in the soil, the calculated value being termed a crop concentration ratios. Generalized crop concentration ratios have been assigned for radium for different crop families (IAEA, 2010). Analysis of these ratios identify that root uptake of radium is likely to be higher than other elements in the uranium or thorium decays series. The IAEA concentration ratios also indicate that the potential extent of uptake can vary considerably. For example in the 77 studies analysed by the IAEA for leafy vegetable uptake of radium, the minimum was 10^{-3} while the maximum ratio was 100, a five orders of magnitude range (IAEA, 2010). This variability can be dependent on a range of soil factors, including the concentration of competing elements in the soil solution or readily exchangeable sites and the soil pH; as well as plant biological variability (IAEA, 2010). Applying the generalized IAEA concentration ratios to establish likely ^{226}Ra activity concentrations in a

country's food supply is difficult, given the variability in uptake from country specific soil types, chemistry, plant cultivation techniques and plant varieties. Across the major growing regions of New Zealand there are range of different soil classifications presenting considerably different soil properties (Hewitt, 2010).

A separate consideration for forecasting uptake into the food supply is that the crop concentration ratio may not be linear with increasing contaminant burden. This may be as a result of alteration in the contaminant fractionation or changes to the soil chemistry from the concurrent presence of other elements. Estimating behaviour of radium from other contaminated sites, such as uranium mine tailings, or naturally elevated regions may therefore under or over-estimate potential uptake (Lauria et al., 2009). The results obtained in Chapter Five enable assumptions on uptake to be formulated through identifying how ^{226}Ra binds to different soil fraction across a range of soil types. To ensure an accurate assessment of the risk of ^{226}Ra accumulation in soil is made it is important to confirm this hypothesis with empirical data.

To assess the food security implications of the ^{226}Ra activity concentrations in New Zealand soils, now and in to the future, it is therefore necessary to directly derive concentration ratios for commonly cultivated agricultural and horticultural crops. These crop concentration ratio can be used to calculate dietary doses that are specific for the New Zealand food supply. The aim of this chapter is to establish any current and future dietary concerns ^{226}Ra in phosphate fertiliser presents through determining crop concentration ratios and the linearity of uptake along a gradient of increasing soil contaminant levels.

6.2. Materials and methods

6.2.1. Crop samples

Food and feed crop samples were taken, as part of a Landcare research study considering cadmium uptake, from the crops grown *in-situ* at the nineteen horticultural and pastoral sites sampled in Section 5.2.2. (Table 6.1.). The cropping sites were distributed across New Zealand (Figure 6.1.; Cavanagh, J., personal communication 01 August 2016). Replicate samples were harvested from duplicate plots at each cropping site to identify any variability. Certain crop species were separated into samples of the different human food and stock feed components, for example potato tuber and skin; or maize cob, leaves and stem. After harvest and separation all samples were oven dried overnight at 62 ^{o}C.

Table 6.1. Crop samples analysed for ^{226}Ra to establish crop uptake factors.

Crop	*n*	Component(s) analysed	Food/Feed
Chicory	1	Foliage	Feed
Clover	2	Foliage	Feed
Lettuce	2	Head	Food
Maize	3	Cob, Leaves, Stem	Food and Feed
Onion	2	Whole bulb	Food
Plantain (*Plantago*)	1	Foliage	Feed
Potato	3	Tuber, Skin	Food
Ryegrass	2	Foliage	Feed
Wheat	3	Grain, Straw	Food and Feed

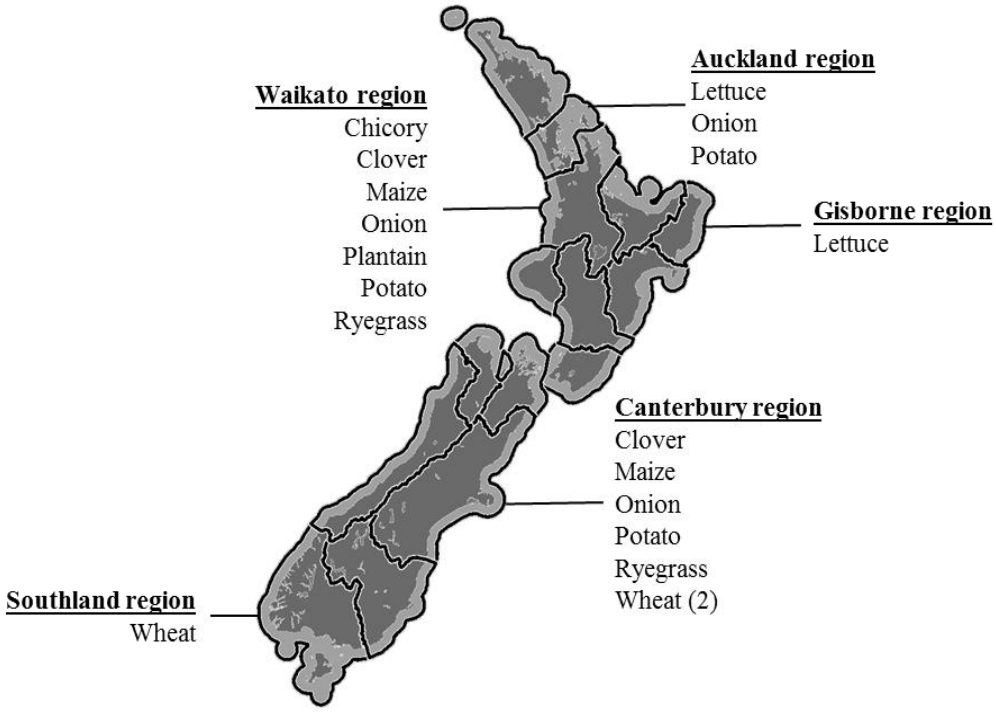


Figure 6.1. Regional distribution across New Zealand of crop sampling sites for ^{226}Ra analysis.

Source: Adapted from Landcare Research, 2016.

6.2.2. Soil gradient samples

A grass airstrip in the Belmont Hills of the Greater Wellington region of New Zealand was sampled to determine if the radium crop concentration ratio remains linear with increasing soil activity concentrations (Figure 6.2.). The site is used for loading and takeoff for planes top-dressing phosphate fertiliser. Although the exact date of commission is unknown, the airstrip has been in use for at least 23 years as it was used for aerial top-dressing of the surrounding land in 1993 (Taylor & Percival, 2001). Previous research undertaken in 2013 had identified a decreasing gradient of uranium contamination down the airstrip starting from the concrete and gravel hard-pan where planes are loaded, adjacent to a fertiliser storage shed (Taylor et al., 2014). The soil

at this location is classified as a firm brown, one of the more common soils in New Zealand (Hewitt, 2010).

Triplicate 10 cm soil cores and ~50 g fresh weight of the associated clover/ryegrass pasture were taken at seven sampling sites at 10 m intervals down a transect of the airstrip (Figure 6.2.). Additionally samples were taken at 15 cm and 1 m points adjacent to the concrete hardpan, where the planes are loaded, and down a runoff gully on the opposite side of the loading pan. These last three sites were selected as previous analysis of the site had identified high levels of phosphate and the contaminants (Cd, F and U) associated with super-phosphate fertiliser (Taylor et al., 2014).

Within 24 hours of collection, pasture samples were washed and oven dried at 85 ^{o}C for 8 hours, a subsample of each of the non-transect foliage samples was weighed prior to drying to determine dry matter content. Soil samples were oven dried in a similar manner to the pasture samples and ground in a mortar and pestle prior to weighing out a 6 g subsample for radium analysis.

In addition to the soils collected in the sampling, two 10 cm soil core samples taken in 1993 were obtained for the 5 m and 45 m marks of the airstrip. The two historical soil cores were analysed for radium to identify the degree of accumulation that had occurred over the last 23 years. Finally the data from 2013 was referred to for establishing gradients for other elements of interest at the sample site (Taylor et al., 2014).

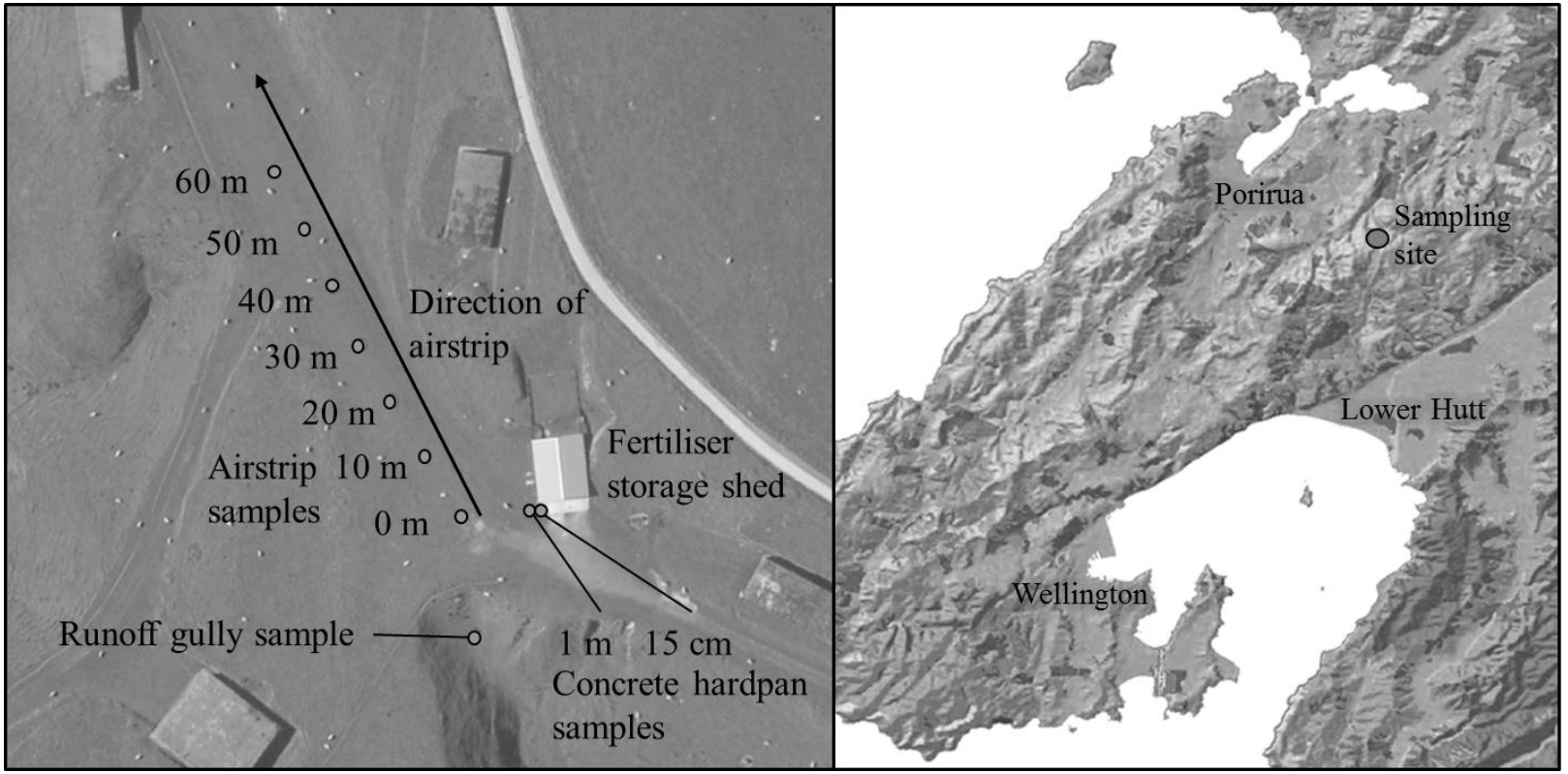


Figure 6.2. Sampling location in the Greater Wellington region of New Zealand with inset showing the sites on the airstrip where soil and foliage samples were collected.

6.2.3. Analysis of radium

All bulk soil samples were hermetically sealed within an epoxy resin using the methodology for bulk soils in Section 5.2.3. After a 30 day in-growth period samples were analysed in a Canberra HPGe gamma spectrometer. ^{226}Ra was indirectly counted through the gamma emissions from ^{214}Pb and ^{214}Bi based on secular equilibrium being maintained. ^{228}Ra was indirectly counted through the gamma emissions from ^{228}Ac.

A minimum crop sample size of 1 g dw was identified as being likely sufficient to obtain suitable method detection levels to quantify ^{226}Ra. Crop samples of between 1 and 10 g dw, depending on the density of the sample, were weighed out into ceramic crucibles. The samples were then ashed at 500 ^{o}C in a muffle furnace, prior to acid digestion with *aqua regia*, a mixture of Fischer Scientific analytical reagent grade nitric acid (69%) and hydrochloric acid (35%). Digests were evaporated to dryness before being reconstituted and separated using the sequential co-precipitation method described in Section 5.2.3.

6.2.4. Data analysis

Quality assurance of the radioanalytical methods was provided through the laboratory's participation in proficiency test exercises organised by the IAEA and the UK National Physical Laboratory (IAEA, 2013a; Dean et al. 2014). Quality control counts were undertaken monthly for the Alpha Spectrometer, with background counts generated as required. For the gamma spectroscopy quality control checks were undertaken monthly on each instrument and three day background measurements conducted every 6 months. Additional steps included matrix spikes to validate methods for the alpha spectrometry and confirming the method accuracy with IAEA proficiency samples. Results for all samples are reported as Bq/kg dw. Minimum Detectable

Concentrations (MDCs) were calculated for each assay according to the method defined by Currie (1968).

Crop concentration ratios for ^{226}Ra were calculated on a dry weight basis using the growing site soil activity concentrations derived in Chapter Five. Equation 6.1. was used to calculate crop concentration ratios. The exception was for the Belmont hills gradient where soil results are reported in Section 6.3.2. Statistical analysis of data was undertaken using Pearson's correlation coefficient.

Equation 6.1.

$$\text{Crop concentration ratios} = \frac{\text{Concentration in the plant (Bq/kg dw)}}{\text{Concentration in the soil (Bq/kg dw)}}$$

6.3. Results and discussion

6.3.1. Crop radium-226 concentration ratios

Duplicate samples of 30 crop commodities were analysed to determine ^{226}Ra activity concentrations. Average tracer recovery was 80% and there was an average difference in ^{226}Ra activity concentration of 17% between duplicates. ^{226}Ra activity concentrations were detected in all of the crops analysed. The levels differed considerably between the crops, with an almost 100 fold difference between the lowest activity concentrations in maize cobs and the highest in plantain (Table 6.2.). Generally the animal feed crops and commodity parts had higher activity concentrations than those for food uses. The pasture species (plantain, chicory, ryegrass and clover) all had the highest ^{226}Ra activity concentrations.

Table 6.2. Mean ^{226}Ra activity concentrations and crop concentration ratios in 30 crop commodities sampled from New Zealand plots, with comparison to the IAEA mean concentration ratio (IAEA, 2014).

Crop (commodity)	Mean ^{226}Ra activity concentration ± u (range) (Bq/kg dw)	Mean ^{226}Ra crop concentration ratio ± u (range)	IAEA mean ^{226}Ra crop concentration ratio
Chicory	2.00±0.51	0.057±0.020	0.069 (Herb)
Clover	1.96±0.61 (1.33-2.56)	0.051±0.021 (0.031-0.072)	0.170
Lettuce	0.57±0.31 (0.48-0.66)	0.012±0.008 (0.007-0.017)	0.066
Maize (cob)	0.09±0.05 (0.07-0.10)	0.002±0.001	0.002
Maize (leaf)	1.05±0.28 (1.03-1.07)	0.024±0.009 (0.024-0.025)	0.018
Maize (stem)	0.39±0.15 (0.36-0.42)	0.009±0.004 (0.008-0.010)	0.018
Onion	0.45±0.18 (0.13-0.84)	0.009±0.004 (0.005-0.020)	0.039
Plantain	8.21±1.23	0.211±0.053	Not specified
Potato (skin)	0.80±0.27 (0.44-1.25)	0.019±0.008 (0.010-0.030)	Not specified
Potato (tuber)	0.18±0.08 (0.11-0.29)	0.004±0.002 (0.003-0.007)	0.009
Ryegrass	3.41±0.82 (1.38-5.43)	0.087±0.029 (0.032-0.143)	0.071
Wheat (grain)	0.20±0.08 (0.18-0.22)	0.005±0.002 (0.004-0.005)	0.017
Wheat (straw)	0.96±0.25 (0.78-1.18)	0.023±0.008 (0.018-0.028)	0.036

Crop concentration ratios were calculated using the growing site soil activity concentrations reported in Chapter Five (Table 6.2.). Comparison to the mean IAEA concentration ratios establishes that for the majority of crops that plant uptake is less than or equal to the international mean

where these have been published (IAEA, 2014). However, for ryegrass whilst the mean was equivalent to the IAEA value one of the crop samples analysed had a concentration ratio double that of the default values. The ryegrass samples also show a large range between the two plots, with the factor that higher crop uptake occurred in the crop grown in the soil with the lower ^{226}Ra activity concentration, similar is also seen for clover, lettuce, onions and the maize cobs and stems. However, for potatoes both the soil and tuber activity concentrations of ^{226}Ra were consistently higher in the one site, being 2-2.5 times that of the soil and tubers at the other two sites sampled. The outcome of this difference across the samples is that there is not a consistent linear relationship between soil activity concentrations and crop concentration ratios for ^{226}Ra. As the data is limited by the number of sites used for growing the crop samples a conclusive trend for each crop is not possible. However, similar decreases in concentration ratios against a soil activity concentration increase have been commonly reported in studies of ^{226}Ra and other naturally occurring radionuclides (Madruga et al., 2001; Martínez-Aguirre et al., 1997; Medley et al., 2013).

In the analysis of ^{226}Ra fractionation in thirteen agricultural soils in Chapter Five, the ratio of soluble and readily exchangeable radium to total radium recovered in all fractions ranged between 0.0013-0.0084. This range of the proportion of exchangeable radium is equivalent to the range of calculated concentration ratios for food crops. However, for forage crops and non- human edible crop parts the concentration ratios are higher. That uptake is not directly equivalent to soluble and readily exchangeable radium in the soil indicates that other accumulation from the other labile soil fractions may be occurring. Analysis through Pearson's correlation coefficient of the CEC values for the soils did not

identify any significant positive or negative correlation to the derived concentration ratios.

For the crops where multiple plant parts have been analysed, maize and wheat, there is a reduced transfer in to the grains against that of the stems and leaves. The observation of limited transfer into grains has been made in other research. A study of uptake into wheat in India reported 22% of total ^{226}Ra activity in the shoots compared to only 2% in the grain (Pulhani et al., 2005). Similarly both ^{226}Ra and ^{228}Ra transfer into winter wheat grain was a tenth of that into the stem (Lindahl et al., 2011).

6.3.2. Soil gradient samples

All of the soils and associated foliage from the samples taken at the Belmont Hills site had detectable ^{226}Ra activity concentrations (Figure 6.3.). ^{226}Ra activity concentrations in the airstrip gradient soils showed an exponential decrease between the sampling points at 0m and 20m. Below the 20m sampling site down the airstrip there was no notable change in the soil ^{226}Ra activity concentrations. Generally the calculated ^{238}U activities were equivalent or less than the ^{226}Ra activity concentrations in the soil.

Analysis of the retained soils from 1993 indicate that considerable accumulation of ^{226}Ra has occurred in the last 23 years at the Belmont Hills site. The analysed ^{226}Ra value from 1993 at 45 m, 36.8±4.3 Bq/kg, is half of that of the 20-60 m 2016 results. Whilst the ^{226}Ra value from 1993 at 5 m, 58±6.2 Bq/kg, is 38% of the 2016 10 m value and 18% of the 0 m value.

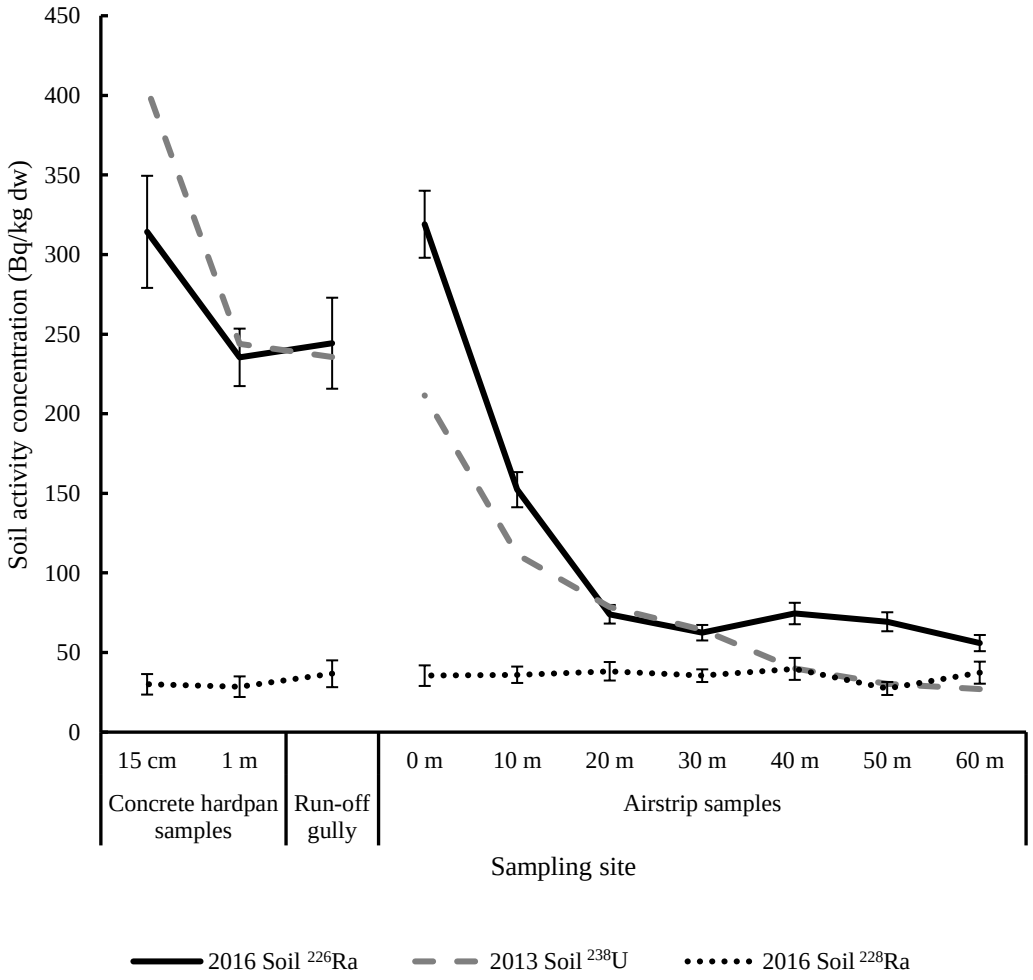


Figure 6.3. Radionuclide activity concentrations in soils taken from sampling sites in the Belmont hills (Figure 6.2.).

In contrast to the ^{226}Ra activity concentrations the ^{228}Ra activity concentrations remained at a similar value in all of the samples, between 27-40 Bq/kg, with a typical uncertainty of 6 Bq/kg. There was no notable correlation to the ^{226}Ra gradient down the airstrip or the high activity concentrations reported in the other three sampling locations. Additionally there is no historical accumulation evident, analysis of the retained soil samples from 1993 gave ^{228}Ra activity concentrations of 37±7-39±8 Bq/kg.

The analysis of the foliage sampled at the Belmont Hills site for ^{226}Ra identified no increases in crop uptake with increasing soil activity concentrations. The ^{226}Ra activity concentrations in the foliage remain consistently within the range of 0.6-1.6 Bq/kg dw, the 15 cm hardpan sample was the highest reported value at 2.4±0.7 Bq/kg dw. As a result of the foliage activity concentrations remaining fixed against the increasing soil activity concentrations the calculated crop concentration ratios for ^{226}Ra increase considerably down the airstrip gradient from 0.004 at the 0 m mark to 0.022 at the 60 m mark. For ^{226}Ra there was a significant log-linear negative correlation between the concentration ratio and soil activity concentration, (R^2 = 0.7828, p = 0.016; Figure 6.4a.)

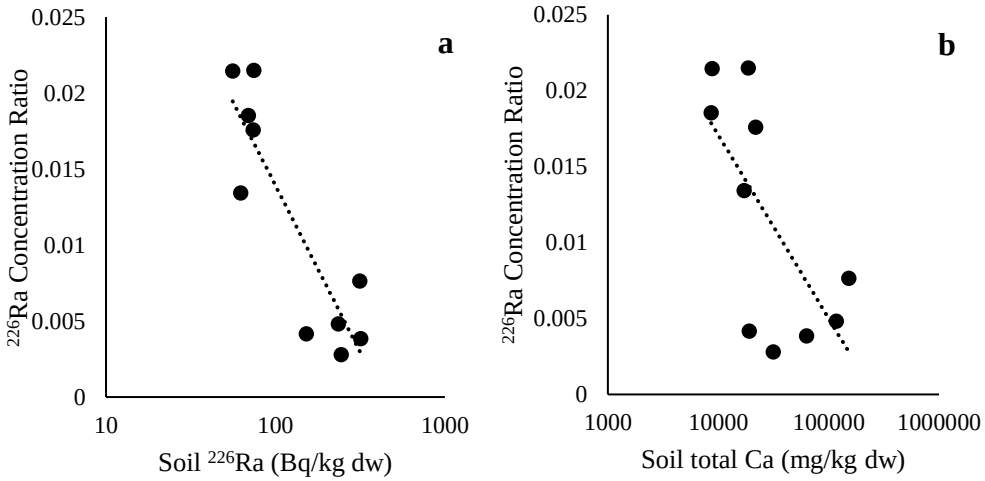


Figure 6.4. Log-linear correlations of ^{226}Ra concentration ratios with (a) total soil ^{226}Ra activity concentrations and (b) soil total calcium, from samples taken in the Belmont Hills site (Figure 6.2.).

A key factor in radium availability for crops is the concentration of competing cations in the soil (Vandenhove & Van Hees, 2007). Analysis of key cation concentrations down the airstrip gradient in the 2013 data indicates these show relative decreases (Taylor et al., 2014). Calcium is

the greatest, decreasing seven fold in concentration between the 0 m mark and the 60 m mark. Sodium and potassium show much smaller relative decrease and magnesium remains unchanged down the gradient. Additionally strontium shows a large relative decrease equivalent to the pattern for calcium.

Negative log-linear correlations are evident for the ^{226}Ra concentration ratio against total soil calcium (R^2= 0.4584, p = 0.048: Figure 6.4b.), total soil potassium (R^2= 0.695, p = 0.013), total soil sodium (R^2= 0.3543, p = 0.043), and total strontium (R^2= 0.5419, p = 0.013). Only for magnesium was there no significant correlation as this remained constant. These negative correlations suggest an influence of competing elements in the uptake of radium into the foliage. Certainly this is supported by the literature with plateauing of radium concentrations in plants hypothesized to occur as root uptake sites become saturated with both radium and high levels of calcium and other alkaline earth metals (Simon & Ibrahim, 1990). However, as there are rising levels of a range of other elements resulting from the fertiliser contamination at this site, there are also significant negative correlations for elements not expected to be involved in radium uptake, such as cadmium (R^2= 0.5466, p = <0.001) and tungsten (R^2= 0.5472, p = 0.019). As a result the certainty regarding the influence of calcium, potassium, strontium and sodium on limiting radium uptake is reduced.

Cation exchange coefficients for these soils were not analysed so it is difficult to interpret this directly as competition from the cations, in particular the bivalent cation Ca^{2+}. However, some degree of competition is likely given the reports in other studies of the inverse relationship between soil calcium and radium uptake (Lauria et al., 2009; Vandenhove et al., 2005).

The results of the soil fractionation presented in Chapter Five are useful in interpreting the lack of linear ratio to the concentration ratio against the soil ^{226}Ra activity concentration. Firstly it is apparent that the additional loading of ^{226}Ra does not result in a relative increase in the ^{226}Ra activity concentration in the readily exchangeable fraction. The additional ^{226}Ra appears to be preferentially bound to organic matter, it is likely therefore that in the Belmont hills soils that as the ^{226}Ra activity concentrations increase up the gradient the excess is bound into the soil organic matter. Additionally with concurrent loading of calcium and phosphates, and a hypothesized increase in barium as a fertiliser co-contaminant, there is the potential that more radium is co-precipitated and thus not in a labile form. In a contaminated site like the Belmont Hills it is likely that a combination of saturation of root uptake, binding in non-exchangeable fractions and co-precipitation will suppress any increase in uptake into crops of ^{226}Ra from fertiliser sources. Research with radiocaesium and radiostrontium has suggested that fertiliser addition may actually be a suitable mitigation method for reducing crop uptake of radionuclides, due to an increased competition for uptake with available calcium and potassium (Shaw, 1993).

It is difficult to confidently apply this hypothesis to all agricultural soils however. Where ^{226}Ra is present in easily exchange or soluble form uptake is more significant. In a study of hydroponic sunflowers (*Helianthus annuus*) the concentration of ^{226}Ra in the seedlings was log-linear to the activity concentration of the ^{226}Ra in the nutrient solution, with a slope indistinguishable from unity (Blanco Rodríguez et al., 2006). Additionally in reports of crop activities from naturally elevated sites there is a greater uptake of ^{226}Ra. For example in a high background activity area of the Islamic Republic of Iran there have been reported activities in fruit crops of upto 1.5 kBq/kg dw (IAEA, 2014). Finally a study

of radium transfer into plants growing on uranium tailings with 7-32 kBq/kg ^{226}Ra was undertaken in the Czech Republic (Soudek et al., 2007). It was reported that wild carrot (*Daucus carota*) had a reported crop activity concentration of 3.7 kBq/kg dw, giving a concentration ratio of 0.21. The high level of ^{226}Ra transferring to these crops indicates uptake can increase proportionally in some soils.

It is probable that a linear increase in crop activity concentrations with fertiliser loading of ^{226}Ra may be highly site specific for agricultural soils in New Zealand. The concurrent application of barium and calcium in the phosphate fertilisers will mean radium is unavailable through co-precipitation in to forms that are not bioavailable, namely low solubility barite or calcium phosphates, which will potentially inhibit a linear increase in ^{226}Ra uptake to crops as soil activity concentrations increase. However, the range of barium and calcium concentrations reported in New Zealand soils is considerable. In a New Zealand survey of 1043 soil samples, of the 0-10 cm horizon, from non-background land uses, barium concentrations were found to range from 15-493 ppm, with a geometric mean of 103 ppm, and calcium concentrations between 400- 31300 ppm with a geometric mean of 3000 ppm (McDowell, 2013). Where the topsoils may be lower in the co-precipitating salts, unless a saturation effect can still occur at these concentrations, then considerably higher ^{226}Ra activities could occur in the cultivated crops.

6.3.3. Current dose estimates from radium-226 and radium-228

An annual ionizing radiation dose can be calculated from the activity concentrations of ^{226}Ra found in Section 6.3.1., through assigning mean consumption values to the crops analysed. Additionally applying the crop concentration ratios to the ranges of agricultural soil ^{226}Ra values established in Section 5.3.3. provides a theoretical range of dietary activities for ^{226}Ra based on the ranges of activity concentrations in New

Zealand soils (Table 6.3.). This relies on the concentration ratio remaining constant with increasing soil activity concentrations, a consideration which is reviewed in greater detail for the forecasting of changes in doses in Section 6.3.4. Applying the crop concentration ratios to ^{228}Ra to estimate its theoretical dose contribution can also be undertaken through this method as they would share the same chemical properties. In studies that have directly compared uptake of both radium isotopes into crops from soil the concentration ratios have been of the same order. For example in analysis of conventional and organic crops all concentration ratios for ^{226}Ra and ^{228}Ra in black beans and lettuce were in the order of 2-4 x 10^{-2}. Only organic carrots showed a large difference in concentration ratios between the two radium isotopes (Lauria et al. 2009). Uptake values for both radium isotopes into winter wheat grain and stems were also equivalent (Lindahl et al., 2011).

The analysis of feed crop concentration ratios gives the potential to estimate the potential dietary burden through animal products. While animal tissues were not analysed in the present study published data from previous animal studies allows an estimation of the accumulation into animal products to be made. A study of cattle and reindeer consuming forage containing ^{226}Ra and ^{228}Ra estimated that 90-95% of the consumed radium is accumulated in the mineral fraction of the bone (Szerbin & Popov, 1988). Additionally in a study of horse and cattle skulls from a higher background activity region of Brazil both ^{226}Ra and ^{228}Ra were found to incorporate at high levels into the bones and teeth (Walencik-Łata et al., 2016). In livestock the bone acts as a sink for the majority of the consumed radium and thus it is removed from the human food supply. It is reported that the tissue accumulation of ^{226}Ra may be primarily limited by the gastrointestinal absorption rate and completion for uptake with dietary calcium (Štrok & Smodiš, 2012). As a result the transfer

factors from feed crop to animal tissues are unlikely to vary to the degree of crop species as the latter can have both soil chemical and physiological influences. To provide an estimate of radium intake from animal tissues the activity concentrations have been extrapolated through the use of the mean transfer coefficients reported by the IAEA of 0.00038 for milk and 0.0017 for meat (IAEA, 2014). Radium activity concentrations resulting from the use of the IAEA transfer factors are sufficiently low it is unlikely that animal products will represent a significant dietary source of radium (Table 6.3.).

Table 6.3. Estimated ^{226}Ra and ^{228}Ra activity concentrations from applying mean concentration ratios and IAEA transfer coefficients to the ranges of soil activity concentrations for New Zealand.

Food	Potential ^{226}Ra activity range for New Zealand (Bq/kg)	Potential ^{228}Ra activity range for New Zealand (Bq/kg)
Onion	0.24-0.79	0.19-0.92
Potato	0.11-0.35	0.08-0.41
Wheat grain	0.14-0.44	0.11-0.51
Lettuce	0.32-1.06	0.25-1.23
Sweet corn	0.05-0.18	0.04-0.20
Milk (pasture diet)	0.001-0.003	0.0008-0.004
Milk (grain/fodder diet)	0.0002-0.0005	0.0001-0.0006
Meat (pasture diet)	0.005-0.015	0.004-0.018
Meat (grain/fodder diet)	0.0007-0.002	0.0006-0.003

Using the estimated activity ranges (Table 6.3.), a dietary model can be constructed for New Zealand age and gender cohorts. The seven food types considered have been mapped to the respective dietary commodities reported on in Chapter Three. Dietary intakes for wheat grain are those

reported on for flour, this being the major semi-processed commodity from wheat grain. As onions were not considered in Chapter Three the intake value for each age and gender group has been derived directly from the 2009 New Zealand Total Diet Study (Vannoort & Thompson, 2010). The activity concentrations estimates for milk and meat from pasture raised animals in Table 6.3. has been used as this is the predominant method for raising livestock in New Zealand (Lincoln University, 2003). To obtain the committed annual dose from the activity concentrations the ICRP ingestion dose coefficients for adults, 15 year old teenagers, 5 year old children and 1 year old toddlers have been used for both ^{226}Ra and ^{228}Ra (ICRP, 1995). The calculation of internal dose coefficients takes into account the following factors: the number of decays during the integration, the decay energy, and the energy deposited to a specific organ from a radionuclide decaying within that organ and in other organs. Considering these factors ^{228}Ra has higher dose coefficients than ^{226}Ra. The primary influences to this difference are that the emitted beta radiation from ^{228}Ra is more likely to penetrate from the bone surface to the sensitive bone marrow than the alpha decay radiation of ^{226}Ra. Additionally with the longer half-life of ^{226}Ra it has greater potential to distribute into deeper areas of bone where tissues are out of the range of its alpha decay particles. (IAEA, 2014).

Calculated dietary ionizing radiation doses show that the teenage age groups have the highest estimates of dose (Table 6.4.). This is as a result of the 15 year age group having a considerably higher dose coefficient for both radium isotopes than other age groups. The primary accumulation site for radium in the body is the skeleton where there is a biological half-life of the activity in adults of 10 years (IAEA, 2014). All non-adult age groups, with the exception of neonates, share the same absorption rate of ingested radium (ICRP, 1995). However in teenage age groups bone sizes

are nearing full adult sizes thus the decay doses remain consistent over the biological half-life of radium in bone. Younger age groups show considerable bone growth as puberty is reached so diluting the skeletal radium and consequently decreasing the committed dose over a lifetime (ICRP, 1993). In Chapter Three the natural radionuclide ^{210}Po was identified as being the significant contributor to dose. However, the high upper bound range of both ^{226}Ra and ^{228}Ra doses suggest that in teenage age groups these may be a more considerable contributor to dose than ^{210}Po. Additionally the lower bound dose estimates for teenage boys and girls for both ^{226}Ra and ^{228}Ra are higher than the UNSCEAR reference values for children of 12 and 40 μSv/yr respectively. (UNSCEAR, 2000)

Table 6.4. Estimated dietary ionizing radiation dose to New Zealand age/gender groupings as a result of estimated ranges of ^{226}Ra and ^{228}Ra activity concentrations in seven foods.

Age/gender grouping	**Estimated dietary dose ranges(μSv/person/yr)**		
	^{226}Ra LB–**RD-**UB*	**^{228}Ra** LB–UB	**^{226}Ra + ^{228}Ra** LB–UB
Adult male (≥25yrs)	4.1-**7.1**-13.4	7.9-38.2	12.0-51.6
Adult female (≥25yrs)	3.0-**5.1**-9.7	5.7-27.8	8.7-37.5
Teenage boy (15yrs)	24.3-**42.2**-79.5	67.1-325.0	91.4-404.5
Teenage girl (15yrs)	20.1-**35.0**-65.9	55.6-269.3	75.7-335.2
Child (5yrs)	7.2-**12.4**-23.4	30.7-148.5	37.9-171.9
Toddler (1yr)	6.4-**11.1**-21.0	29.7-144.0	36.1-165.0

* LB: Lower-bound; RD: Reported Dose - The calculated dose from the reported activity concentrations of ^{226}Ra in the crops sampled in Section 6.3.1.; UB: Upper bound.

The doses for all age groups are predominantly driven by the radium activity concentrations in wheat grain, at 86 – 92 % the total dose. Whilst meat and milk are both consumed in large quantities, in the modelled diets the transfer of radium activity is very low leading to a less significant dietary contribution. The importance of grain to the radium dose has been

reported in other studies. For example, in a study of natural radionuclide uptakes in to wheat in India, the adult dose from ^{226}Ra in grain alone was estimated at 18.4 μSv/yr (Pulhani et al., 2005).

6.3.4. Contribution from TeNORM and forecast of future increases

In Chapter Five it was established that ^{226}Ra activity concentrations had likely elevated over background soils levels as a result of fertiliser inputs. As a result the contribution of ^{226}Ra to the diet cannot be considered as entirely background with a proportion of the dose being of anthropogenic origin. Establishing this proportion is important as it is considered against the reference dose level of 1 mSv/yr, adopted for dietary risk characterisation in Section 3.2.2. Only for potatoes in Section 6.3.1. is there an increasing crop activity concentration as soil activity concentrations of ^{226}Ra increase. For all of the other crops there is a general trend for concentration ratios to decrease inverse to soil ^{226}Ra activity concentrations as the plant activity concentrations remain static or decrease. This inverse trend is reinforced by the lack of increase in the pasture sample activity concentrations against the soil gradient of ^{226}Ra in Section 6.3.2.

Making an allowance for the potato concentration ratio remaining linear with increasing soil activity concentrations the difference in dose as a result of an anthropogenic elevation in soil of ^{226}Ra can be calculated. The Wellington native soils analysed in Chapter Five have been adopted as the baseline for natural ^{226}Ra soil activity concentrations for New Zealand. This value is also consistent with the soil activity concentrations from the soil studies undertaken in the 1970s (Baltakmens, 1976; Dobbs & Matthews, 1976). As a result of the increase from the baseline to the current New Zealand mean agricultural soil activity concentration ranges, the additional dose received from potatoes increases between 0.14-1.17 μSv. Applying this value to the last 40 years of soil accumulation of ^{226}Ra,

the annual increase in dietary dose is at most 30 nSv/yr. This is an insignificant increase when compared to the concurrent decrease over the last 50 years in the dose from fission products in the diet. With the ^{90}Sr and ^{137}Cs annual dose though consumption of milk alone for an adult being estimated in Chapter Three to have decreased 82.3 μSv.

A key use for the collected research data on the behaviour of ^{226}Ra is to forecast if continued soil loading through fertiliser will result in a scenario where dietary doses exceed the reference dose level. With the data collected in this chapter there are two forecasts possible for the behaviour of ^{226}Ra in soil. The first is for the concentration ratios to decrease relative to the increase in soil activity concentration, thus leading to no net gain in activity concentrations entering the diet. The experimental data from the soil gradient at the Belmont Hills site supports this scenario, with ^{226}Ra remaining at a consistent activity concentration in the foliage despite the increasing soil ^{226}Ra concentration. Additionally given the soil partitioning results in Section 5.3.4. this may best reflect the behaviour of fertiliser origin ^{226}Ra in agricultural soils due to the suspected immobilization in precipitates with barium and calcium. Clearly from a food security outlook this is the most desirable outcome as with this scenario the dose from ^{226}Ra in the diet will remain constant and unlikely to require any future regulatory action.

There are indications in the concentration ratios, notably for potatoes, that a decreasing concentration ratio as a function of the soil ^{226}Ra activity concentration cannot be assumed for all crops. As noted in Section 6.3.2. the results from the Belmont Hills site may also be an artefact of the suppression of uptake with the high levels of competing cations and sufficient calcium, phosphate and barium to allow co-precipitation to occur. In sites subject to a more gradual loading there may be sufficient time for precipitates to solubilize, or increases in competing elements to

be insufficient to fully suppress an increase in radium crop uptake. A scenario accounting for this would be that over time the concentration ratios remain static and so crop activity concentration increase proportionally with soil activity concentrations.

In Chapter Five an annual increase rate of 0.58 Bq/kg was reported from the accumulation of soil ^{226}Ra over the last 40 years. This rate is slightly higher than the reported uranium loading rate of 0.41 Bq/kg ^{238}U in New Zealand soils by Taylor (2007). It however fits well with the calculated loading of 0.54 Bq/kg ^{238}U occurring as a result of application of 50 kg P/ha year to pastoral land (Schipper et al., 2011). By anticipating that the annual loading of ^{226}Ra to soil continues at 0.58 Bq/kg it is possible to calculate the increase dose that would result (Table 6.5.). The assessment has been undertaken using the teenage boy age/gender cohort as this is the age/gender cohort with the highest dietary doses from ^{226}Ra (Table 6.4.). A limitation of this model is that future dietary practices are anticipated to remain unchanged from those reported in the 2002 New Zealand Child Nutrition Survey (MOH, 2003). Finally the model assumes that sources and application rates of fertilisers will remain constant. Manufacturers sourcing different phosphate ores or a shift in use to different phosphate products may alter the rate of long-term loading.

As presented in Table 6.5. even with 500 years at the current rate of loading of ^{226}Ra to soil from fertilisers the additional dose over baseline only constitutes 28% of the adopted reference dose level of 1 mSv/yr. Using this forecast it would be necessary to undertake regulatory action on New Zealand soils only after 1,900 years.

Table 6.5. Forecast future increases to soil ^{226}Ra mean activity concentrations based on an annual loading rate of 0.58 Bq/kg, with the calculated additional dietary ionising radiation dose to male teenagers over the current baseline.

	Number of years of forecasted soil increases of ^{226}Ra				
	10	**50**	**100**	**250**	**500**
Mean soil activity (Bq/kg)	51.8	75	104	191	336
Additional dose over baseline (μSv/yr)	21.8	42.6	68.8	147.3	277.9

An additional increase in the dose from ^{238}U, ^{234}U, thorium-230 (^{230}Th), ^{210}Pb and ^{210}Po is possible as these will also undergo soil loading through phosphate fertilisers. However, similar to ^{226}Ra, the concentration ratios in plants are unlikely to increase linearly with increasing soil activity concentrations (Sheppard & Evenden, 1988). Anticipating that the soil activity concentrations of the decay series from ^{238}U to ^{226}Ra will remain in secular equilibrium is straightforward, although there are certain factors such as occurrence as more soluble species, alpha-recoil ejection and change in oxidation states that could lead to greater leaching from top soil of the parent and grand-parent radionuclides to ^{226}Ra (Suksi et al., 2006). It is possible to undertake a conservative forecast for the increasing dose from annual soil loading with ^{238}U, ^{234}U and ^{230}Th activity concentrations of 0.58 Bq/kg. Using IAEA concentration ratios for uranium and thorium in the crops and animal products of interest and the appropriate ICRP dose conversion factor for ^{238}U, ^{234}U and ^{230}Th the estimated dose can be calculated (IAEA, 2010; ICRP, 1995). The sum of the dose from ^{238}U, ^{234}U and ^{230}Th equates to 17% of that resulting from ^{226}Ra. As a result the forecasted combined dietary dose from soil loading of ^{238}U,

^{234}U, ^{230}Th and ^{226}Ra in secular equilibrium only exceeds the adopted reference dose level of 1 mSv/yr after 1,600 years.

Assuming secular equilibrium will be maintained in soils for the radionuclides following the decay of ^{226}Ra is far less certain due to the emanation and atmospheric loss of ^{222}Rn. As well as the potential for the import to the soil through fallout from external sources of the airborne daughter radionuclides of ^{222}Rn. This latter source, as well as emanation of ^{222}Rn from elevated soil activities, may also introduce foliar deposition and absorption as a source of uptake to cultivated crops. As a result it is concluded that there are too many variables to provide a robust estimate on dose from the increased ^{210}Pb and ^{210}Po that may result through soil loading from phosphate fertilisers.

It has not been established if the apparent elevation of ^{228}Ra activity concentrations in New Zealand soils, reported in Chapter Five, is due to anthropogenic inputs. However, if the annual loading rate of 0.4 Bg/kg ^{228}Ra calculated from Section 5.3.3. is a result of technological enhancement the timeframe for regulatory action, based on exceeding an annual dietary dose of 1 mSv, would be 750 years. A shorter timeframe than with ^{226}Ra, however still unlikely to represent a risk to human health requiring near-term management.

6.3.5. Other radiological considerations

Whilst the food safety impacts of topsoil loading with ^{226}Ra is unlikely to constitute a regulatory issue there is another significant radiological risk to consider. This risk is the emanation of ^{222}Rn from these soils, particularity if land use changes from agriculture to residential. In such a scenario the hypothesized presence of ^{226}Ra in barium or calcium co-precipitates may increase the risk as it will allow for greater resistance to weathering and greater retention in top-soils.

The only regulatory limit sighted worldwide for soil radium is that of the US EPA in relation to tailings from uranium and thorium mining (40 C.F.R § 192, 2016). The stated limit for topsoil is 5 picoCurie/g, equivalent to 185 Bq/kg, over background for total ^{226}Ra and ^{228}Ra. An estimate for the New Zealand background activity concentration for both radium isotopes can be taken from the native forestry sites analysed in Section 5.3.2. If ^{228}Ra remains static, at the current mean activity concentration and rate of increase for ^{226}Ra in agricultural soils the regulatory limit would be exceeded in 260 years. A continuous increase of both radium isotopes from the current mean agricultural soils activity concentrations however would have this limit exceeded in 155 years.

6.4. Conclusion

To establish the dietary risk of ^{226}Ra accumulating in New Zealand agricultural soils, from phosphate fertiliser use, a range of concentration ratios have been derived for common agricultural and horticultural crops. The values indicate that uptake of ^{226}Ra into food crops is low and compares well with the default IAEA values. Dietary burden assessment of ^{226}Ra, and by extrapolation of concentration ratios ^{228}Ra, indicates radium represents a large component of the dietary ionizing radiation dose, particularly in teenage age groups. The calculated dose is largely driven through consumption of wheat based foods.

Analysis of foliage samples along a gradient of ^{226}Ra soil activities indicates that uptake into plants remains fixed, as a result plant concentration ratios decrease in higher activity soils. The implications of this for dietary dose are that even with the accumulation identified in Chapter Five of ^{226}Ra in soil over the last 40 years the additional dietary dose is minimal. Forecasting of the future dietary ionizing radiation dose has been undertaken to understand if there is a future risk to health from fertiliser origin ^{226}Ra loading in agricultural soils. It is most probable that

fertiliser applied ^{226}Ra will be in a form unavailable for root uptake due to co-precipitation with barium or calcium salts, thus no increase in dose is expected. Using a conservative assessment where plant uptake is linearly correlated to the increasing soil activity concentration, at the historical rate of soil loading of ^{226}Ra the future timeframes for a health concern to manifest are extensive. It is concluded that although phosphate fertiliser use in New Zealand will increase the soil activity concentrations of ^{226}Ra this does not manifest as a food security concern requiring mitigation in the foreseeable future.

Chapter 7 - Conclusion

7.1. Summary of the research

This is the first New Zealand research to comprehensively analyse the New Zealand diet for radionuclide activity and calculate the resulting ionising radiation dose. Annual monitoring had been undertaken since the 1960s of milk for the anthropogenic radionuclides ^{90}Sr and ^{137}Cs (Matthews, 1993). However, there was no data on these radionuclides, or other radionuclides of natural and anthropogenic origin across other foods in the diet. This thesis has contributed to addressing many of the data gaps in the radiological status of the New Zealand diet. The current activity concentrations for key radionuclides in important New Zealand dietary foods have been established. These activity concentrations have allowed an estimate of the dietary committed doses for ionising radiation to the New Zealand population to be calculated.

Using the baselines for current dietary ionising radiation exposure as a foundation the research has explored if there are short and long term risks of increased activity concentrations of radionuclides entering the diet. Both near-term increases of ^{137}Cs in seafood and long-term increases of ^{226}Ra in agricultural crops have been identified as being of negligible dietary concern. As a result, the dominant current, and probable continuing, dietary contributors for the New Zealand population are the natural background radionuclides ^{210}Po, ^{226}Ra and ^{228}Ra. The conclusion of this research is that food security in New Zealand is strongly insulated against many sources of radiological risk. This conclusion can be further reinforced through investigation of some of the further research streams proposed in Section 7.4.

7.2. Summary of objectives and outcomes

7.2.1. Gather data to support establishment of radionuclide baselines and a refinement of the dietary radiation dose for the New Zealand population

Chapter Two reports on a survey of radionuclide activity concentrations across the New Zealand diet. This survey was undertaken to better understand the radioactivity content of the modern diet and also to assess the suitability of the current use of milk as a sentinel for dietary radionuclide trends. Thirteen radionuclides were analysed in 40 common food commodities, including animal products, fruits, vegetables, cereal grains and seafood. Activity was detected for ^{137}Cs, ^{90}Sr and ^{131}I. No other anthropogenic radionuclides were detected. Activity concentrations of the three natural radionuclides of uranium and the ^{238}U daughter radionuclide ^{210}Po were detected in the majority of foods sampled, with a large variation in magnitude. Shellfish had the highest activity concentrations detected for all these radionuclides. Based on the established activity concentrations and ranges, the New Zealand diet contains activity concentrations of anthropogenic radionuclides well below the Codex Alimentarius guideline levels. Activity concentrations obtained for milk support its continued use as a sentinel for monitoring fallout radionuclides in terrestrial agriculture. The significant levels of natural and anthropogenic radionuclide activity concentrations detected in finfish and molluscs support undertaking further research to identify a suitable sentinel for New Zealand seafood monitoring.

Using the derived activity concentrations dietary modelling was undertaken in Chapter Three for different age and gender groupings of the New Zealand population. Deterministic and semi-probabilistic models were constructed to derive estimates of the committed dose of ionising radiation via the diet. Deterministic models estimated that annual doses

ranged from 48-66 μSv/yr for teenage girls, to 126-152 μSv/yr for adult males. The main contributor to ingested dose was ^{210}Po, with anthropogenic radionuclides contributing very little. For adults, seafood represented the most important source of exposure, with the contribution from this source diminishing in the younger age groups. Results of the semi-probabilistic model showed a range of possible ingested doses, with the mean annual doses being calculated at 62.1-80.4 μSv/yr for adults, and 91.3 -127.8 μSv/yr for children. Estimated doses to the New Zealand population show similarities to those of other countries and fall within the expected global range.

7.2.2. Gather data to quantify the potential short- and mid-term risks to enhancement of the dietary radiation dose

Chapter Four reports on a survey undertaken to determine activity concentrations for ^{134}Cs, ^{137}Cs and ^{210}Po in New Zealand seafood, and establish if activity concentrations varied with respect to species/ecological niche and coastal region. Thirty seafood samples were obtained from six fishing regions of New Zealand, and a further six samples of two commercially important species (hoki and arrow squid) with well-defined fisheries, were obtained. ^{134}Cs was not detected in any sample. However, ^{137}Cs was detected in 47% of samples, predominantly in pelagic fish species, with most activities at a trace level, and no regional-specific trends. Activity concentrations were consistent with those expected from the oceanic inventory representing residual fallout from global nuclear testing. In comparison, ^{210}Po was found above the minimum detectable concentration in 33 (92%) of the analysed samples, molluscs displayed significantly elevated activity concentrations relative to all other species groups. No significant regional variation in ^{210}Po activity concentrations were determined. Subsequently, two dose assessment models for high seafood consumers were undertaken. Dose contribution

from ^{137}Cs was minimal and far below the adopted reference dose level of 1 mSv/yr, while exposure to ^{210}Po was significant in high seafood consumers at 0.44-0.77 mSv/yr (5th-95th percentile). As a result of its low dose contribution ^{137}Cs is unlikely to represent a source of near-term dietary risk. However, ^{137}Cs is concluded to be a valuable sentinel radionuclide for monitoring anthropogenic releases, such as global fallout and reactor releases, in the marine environment. ^{210}Po is of importance as a natural radionuclide sentinel due to its high contribution to dietary committed dose in seafood consumers.

7.2.3. Quantify the factors influencing radiological risk, and forecast the future threat, to agriculture from phosphate fertilisers

Phosphate ore sources worldwide can contain high levels of ^{238}U and its decay products, of which ^{226}Ra is an important environmental contaminant. ^{228}Ra from ^{232}Th decay may also be present, but at lower activity concentrations. For many countries, the acid processing of phosphate ore to triple superphosphate elutes a large proportion of the ^{226}Ra from the final product. In contrast, New Zealand generally uses single superphosphate and reactive phosphate rock to maintain crop yields. These fertilisers do not undergo an elution step during manufacture and ^{226}Ra is retained in the final product.

In Chapter Five it was reported that significant activities of ^{226}Ra are present in phosphate-containing fertilisers used in New Zealand, ranging up to 1.6 kBq/kg, however ^{228}Ra did not exceed 75 Bq/kg. Subsequently, analysis of 40 New Zealand soils, covering a range of land uses, showed activities of between 27-88 Bq/kg ^{226}Ra and 21-102 Bq/kg ^{228}Ra. Both radium isotopes show apparent elevation over the results of soil monitoring undertaken in the 1970s (Baltakmens, 1976; Dobbs & Matthews, 1976). Unexpectedly, there was also a strong correlation between the two radium isotopes. In 13 of the agricultural soils, all with

very high phosphate levels, the partitioning of ^{226}Ra was determined, indicating that it largely remains immobile in the residual phase of the soil. It is hypothesised that a large proportion of the ^{226}Ra activity concentration is not bioavailable as it is co-precipitated with calcium phosphate or barium sulphate, the latter having very low solubility in environmental conditions.

In Chapter Six agricultural soil and crop pairings were analysed for ^{226}Ra to establish transfer factors. For all food crops and some feed crops, the calculated transfer factors fall within 0.005-0.05 g/g, although certain pasture crops ranged up to 0.2 g/g. Dietary burden analysis indicates ^{226}Ra and ^{228}Ra exposure is largely through cereal grains. Soils and foliage from a fertiliser-contaminated site were analysed to establish plant uptake along an increasing ^{226}Ra soil activity. Plant uptake did not increase as a result of increasing soil activity concentrations. Future increases to the dietary ionising radiation dose were forecast using the current fertiliser inputs of ^{226}Ra to agricultural soils. This forecasting estimated it will take more than a thousand years to reach a dose requiring regulatory intervention.

7.3. Applications and recommendations

An outcome of this research was establishing current activity ranges of radionuclides, both in the diet and in agricultural soils. These values have strong applications as baselines for future monitoring. It is important, therefore, to not cease surveys for radionuclides in the diet based on the results obtained in this thesis. Repeat surveys are recommended to establish trends in activity concentrations and to confirm a number of the forecasts made in this thesis. A robust New Zealand food monitoring program already exists in the form of the New Zealand Total Diet Study (Vannoort & Thompson, 2009). Consideration could be placed on the inclusion of a radiochemical aspect into future surveys as a tool to

monitor long-terms trends in dietary doses. Adding other sentinel foods, such as a seafood species, to the current annual monitoring programme would also be of value in complementing the trend monitoring. To ensure global research access to New Zealand radionuclide dietary occurrence values all the activity concentrations have been uploaded into the World Health Organization Global Environmental Monitoring System.

A further outcome was the determination that ^{226}Ra, and potentially ^{232}Th, activity concentrations in soil appear to be increasing. Whilst this thesis indicates the long-term food safety implications of this increase are low, an aspect not directly considered is the health impact of an increased inhalation dose from radon. ^{222}Rn is the decay daughter of ^{226}Ra and as a noble gas can emanate from the matrix where its parent is present. In confined areas, such as basements, ^{222}Rn emanation allows a build up to air concentrations of potential health concern. Some New Zealand soils, particularly those in proximity to fertiliser storage, would likely exceed the US regulatory limit for soil radium (40 C.F.R § 192, 2016). New Zealand currently has a low risk of radon in dwellings and work places (Randle, 2001). Maintaining this status is seen as advantageous in limiting the ionising radiation dose to the population and minimising the costs of mitigation measures in dwellings. It is therefore recommended that consideration be placed on deriving a soil guideline level for ^{226}Ra in New Zealand soils, particularly to manage change in land uses to residential housing.

7.4. Future research

As a result of this thesis a number of opportunities have been identified for further research. These will be complimentary to the efforts described herein characterising the radiological status of New Zealand food.

7.4.1. Radionuclide contamination of waste streams

The finding of ^{131}I in shellfish in Chapter Two highlights the potential for nuclear medicines to enter the food chain. The extent to which this occurs is unknown, both in New Zealand and internationally. ^{131}I is only one of a suite of radionuclides used in medical diagnostics and therapies in New Zealand, with others including ^{51}Chromium and ^{99m}Technetium (Beach, 2005). Additionally, there is the potential for other applications of radionuclides, or waste material from NORM industries, to enter municipal waste streams. While direct output into the marine environment is one route of entry of waste stream radionuclides into food chains, other routes may include applications of biosolids (organic waste based soil conditioners and composts) to land, or volatilisation from waste storage ponds or piles.

The presence of detectable activity concentrations in individual foods, while unlikely to be an acute health risk in all but extreme activities, could result in increased dose burdens over a lifetime. This is particularly relevant if contamination is present in a food with limited zones of cultivation. Such as oysters, in which the ^{131}I activity was detected in Chapter Two. Additionally, there could be trade implications if an unexpected radionuclide activity is detected by an international trading partner.

Establishing the frequency of radionuclide outflow into waste streams, and the proximity to food production areas, will allow the risk to be better characterised and, if necessary, allow mitigation methods to be implemented. It is also possible that radionuclide contamination of waste streams may present a convenient marker for rapid testing of foods for potential faecal or other microbiological contaminants also present in the waste streams.

7.4.2. Temporal and spatial patterns of polonium-210 variation in shellfish

The results from Chapter Four suggest the presence of considerable natural variation in ^{210}Po activity concentrations amongst shellfish species. The regional sampling programme undertaken was not specific enough to elucidate if spatial or temporal factors may play a part in this variation for New Zealand species. Certainly, some international studies have attributed factors such as seasonal changes in the physiology of the species (e.g. spawning) is a noted source of variation (Wildgust et al., 1998). Additionally, growing sites near estuaries or other areas of large surface run off may receive greater activities of ^{210}Po from surface waters in comparison to seawater (Aközcan & Uğur Görgün, 2013) meaning that harvesting location may be an important factor explaining variation.

While ^{210}Po is a normal component of the diet, establishing the variance in natural ranges would be of importance in identifying and managing industrial releases of NORM to the environment. At the time of undertaking the research for Chapter Four, a proposed environmental consent application was underway to mine sea-floor phosphorite nodules for fertiliser use (EPA, 2015). Although consent to mine was not granted, concerns were raised over the uncertainties regarding disturbance of ^{238}U decay series-containing material and waste product in relation to contamination of marine species (EPA, 2014).

Given the propensity of ^{210}Po to concentrate in marine species, being able to identify any excess over normal background ranges for a certain area or time of year may prove a useful tool. In particular, this will be beneficial for identifying, and potentially regulating, the non-natural contribution to the ionising radiation dose (e.g. that caused by mineral extraction). It is conceivable, given the high dose conversion factor for ^{210}Po, that NORM sources could lead to ingested activity concentrations

that exceed the 1 mSv/yr reference dose level and therefore require mitigation. Certainly this has been reported overseas, for example at Whitehead in the United Kingdom (CEFAS, 2014).

7.4.3. Thorium-232 soil and crop activity concentration ranges

An unfortunate omission from this thesis, with the exception of some soil reporting on ^{228}Ra in Chapter Five, has been activity concentrations of radionuclides from the ^{232}Th decay series. The radiochemical method for ^{232}Th analysis of food or crop commodities was not able to be conducted within the timeframes of the research. This was partly due to analytical difficulties with attempting to quantify activity concentrations on a mass basis through ICP-MS. Given these problems, the low dose conversion of ^{232}Th, and the lower contribution it makes to dose calculations internationally, it was thus excluded from the dietary monitoring (ICRP, 2012; UNSCEAR, 2000). As the thesis research progressed to monitoring soil samples, the unavailability of ^{232}Th data proved to be unfortunate. The ^{228}Ra results in Chapter Six indicated that a range of ^{232}Th activity concentrations are present in agricultural soil, potentially in excess of the historical values. The resulting uptake into the food supply of this ^{232}Th is, therefore, unknown. Consequently, it has not been possible in this thesis to address whether this ^{232}Th is of wholly natural origin, or whether certain agricultural practices could be resulting in its increase. The case for the dietary significance of the daughter ^{228}Ra has already been made in Chapter Six, however the rapid progression through the decay series after thorium-228 also makes this important for internal exposure as multiple ionisations may occur. Dedicated research to determining inputs of ^{232}Th would therefore be of benefit in completing the picture of the future radiological risks to New Zealand.

7.4.4. Co-precipitation of radium with barium sulphate

During the fractionation study in Chapter Five, a very high proportion of ^{226}Ra was present in the residual fraction. This was hypothesised to be a result of co-precipitation of the radium with barium sulphate. This would potentially occur as a result of the sulphuric acid treatment in the fertiliser manufacturing. If this is the case a large proportion of the ^{226}Ra activity in fertilisers would likely be in the form of a low solubility precipitate prior to its addition to land. This would reduce the ^{226}Ra available for plant uptake, thus limiting the dietary risk. However, it may increase the persistence of ^{226}Ra in topsoil, and thus sustain an increase in ^{222}Rn emanation. This latter scenario would increase the risks resulting from land conversion, potentially necessitating mitigation measures.

Identifying the degree of ^{226}Ra co-precipitation occurring with barium sulphate would therefore be a valuable investigation. The experimental work could include quantifying concentrations of barium in phosphate rock in New Zealand. In an Australian study where high soil sulphates were expected, an additional stage was added to the sequential extraction method to quantify sulphate co-precipitates. (Medley et al., 2013). EDTA was used at an alkaline pH to dissolve the barium sulphate precipitate. A similar addition could be included to the sequential extraction of New Zealand phosphate ores and soils to identify if this fraction holds significant activity concentrations of ^{226}Ra.

7.4.5. Modelling future risks based on geopolitical scenarios

The modelling work around future risks in this thesis has been based around established sources of radionuclides that may impact on the New Zealand supply. To be able to comprehensively anticipate all probable risks for dietary ionising radiation exposure to the New Zealand diet it is necessary to evaluate more speculative scenarios. These are predominantly geopolitical developments, such a recommencement of

nuclear testing or hypothesising for future expansion of nuclear power into the Southern Hemisphere, for example into Indonesia or Australia. Anticipating for such eventualities and modelling based on the baselines established for the New Zealand diet in this thesis will further enhance the potential to protect from dietary risk from radionuclides.

7.5. Concluding remarks

Geographic isolation and a lower industrial density (nuclear and non-nuclear), contribute to a degree of insulation from radionuclide entry to the New Zealand environment. This presents a positive prognosis for New Zealand in the Modern era in terms of radiological risk to the diet. Being able to communicate a positive food security outlook is noteworthy as the perception of radiation risk by the general public is often significantly higher than that of experts (Perko, 2014).

The 1955 Mainau declaration that opened this thesis portrays the collective scientific alarm into the health effects of fallout following a war fought with nuclear or thermonuclear weapons, a situation that has thankfully not yet come to fruition. Whilst the threat of nuclear war persists to the current day, the health concerns of fallout from the above-ground testing conducted in that era, have largely dissipated for New Zealand.

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Appendix A – Example spectra

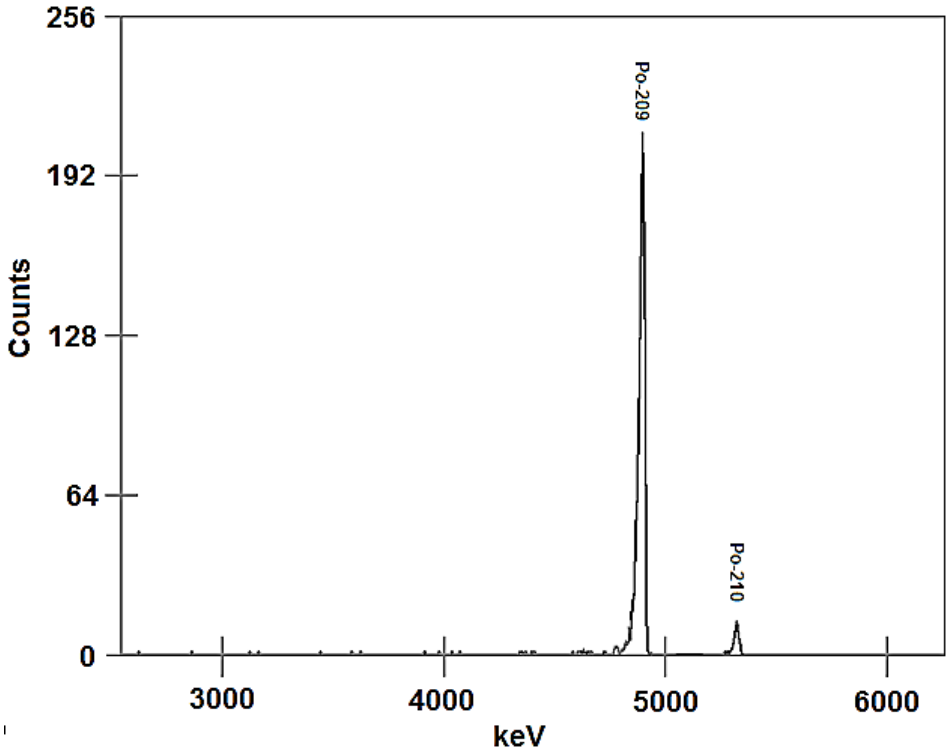

Figure A.1. Spectra of the alpha emission peak for ^{210}Po (5.3 MeV), and the yield tracer ^{209}Po (4.8 MeV), in the analysis of ^{210}Po in food samples.

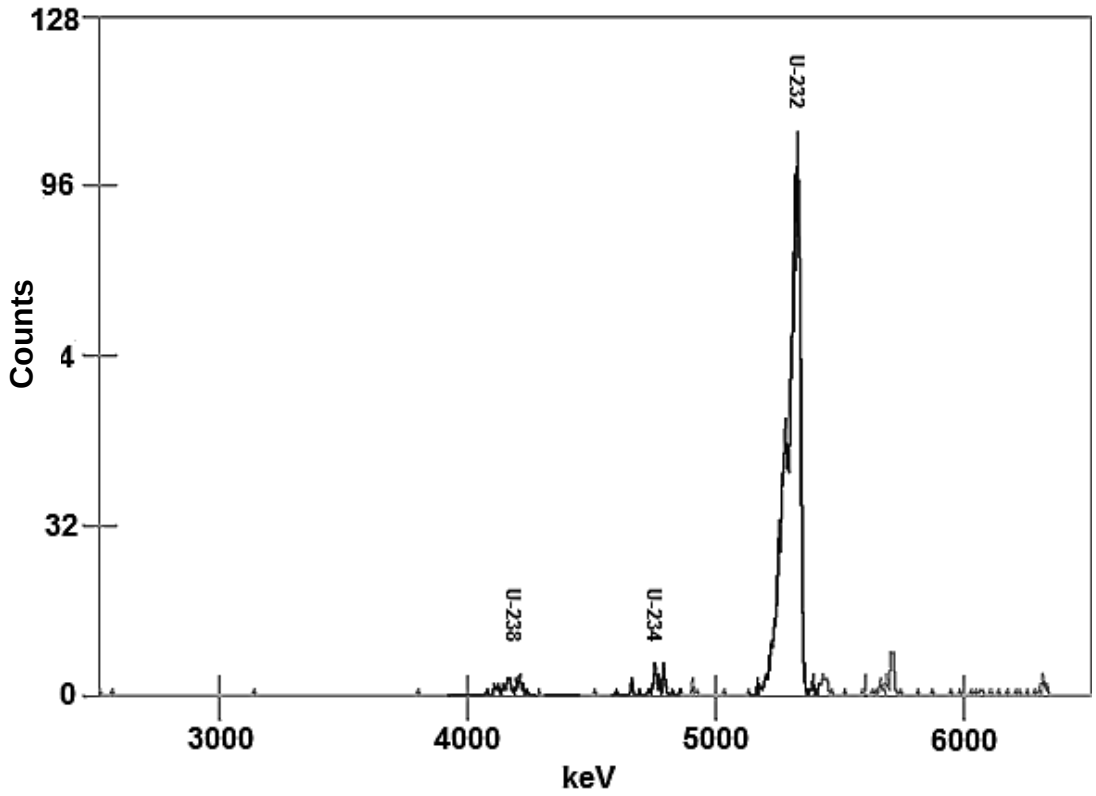

Figure A.2. Spectra of alpha emission peaks for ^{234}U (4.8 MeV) and ^{238}U (4.2 MeV), and the yield tracer ^{232}U (5.3 MeV), in the analysis of food samples for uranium isotopes. A peak at 4.4 MeV would signify activity of ^{235}U.

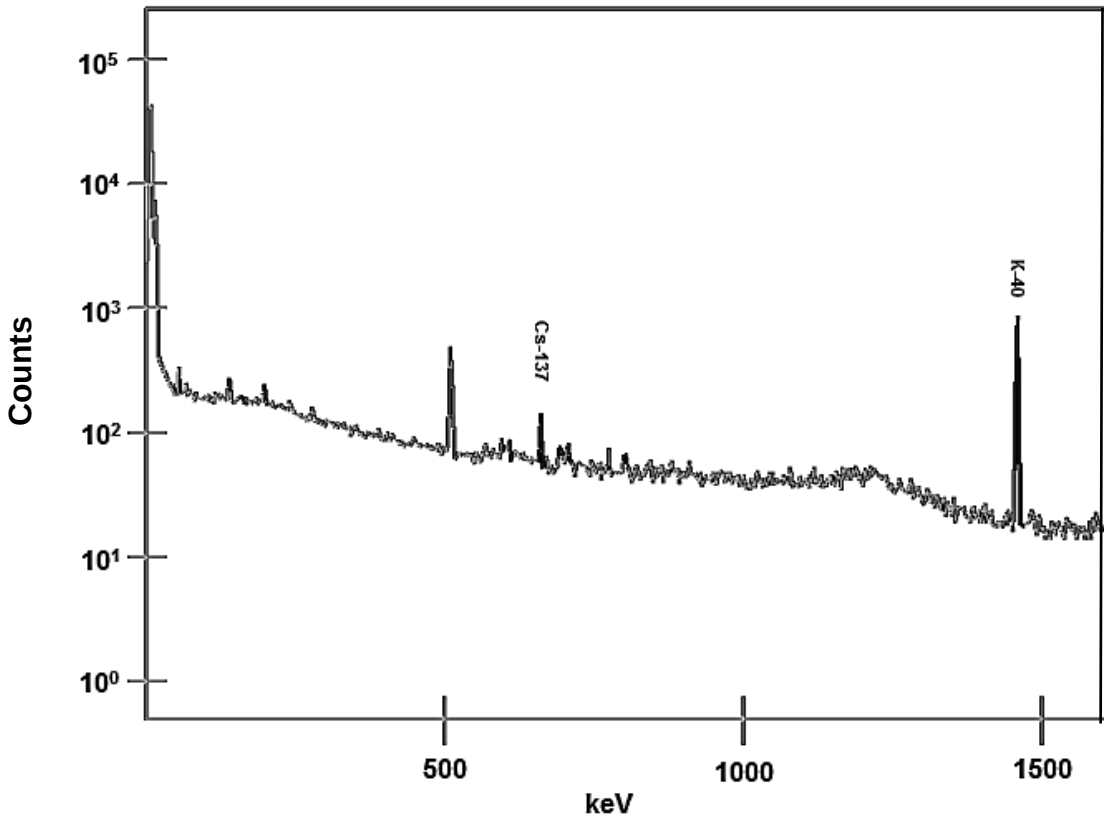

Figure A.3. Spectra of the ^{137}Cs gamma emission peak (662 keV) in the analysis of seafood samples for gamma-emitting radionuclides. The gamma emission peak for ^{40}K (1461 keV) is also highlighted.

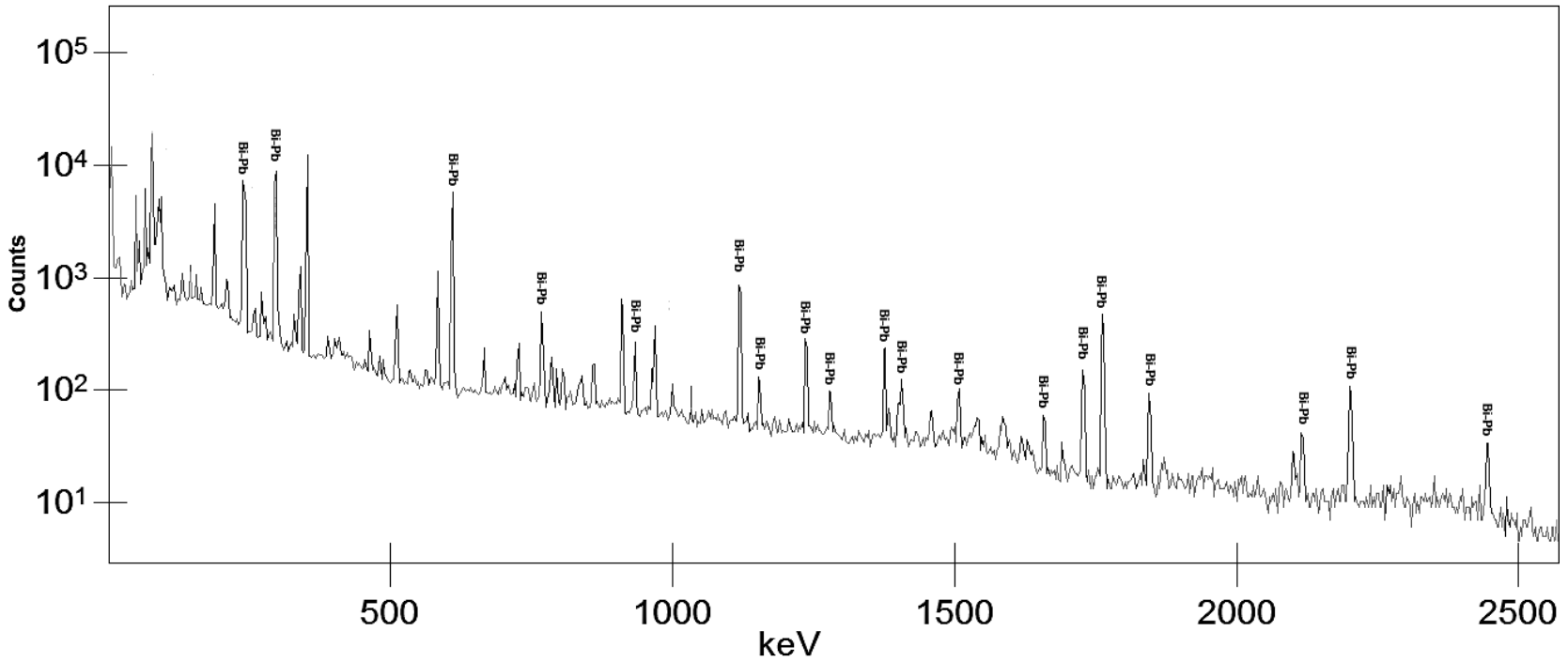

Figure A.4. Spectra of ^{214}Bi and ^{214}Pb gamma emission peaks, with a gamma emission yield per disintegration of >1%, in the indirect measurement of ^{226}Ra in a fertiliser sample.

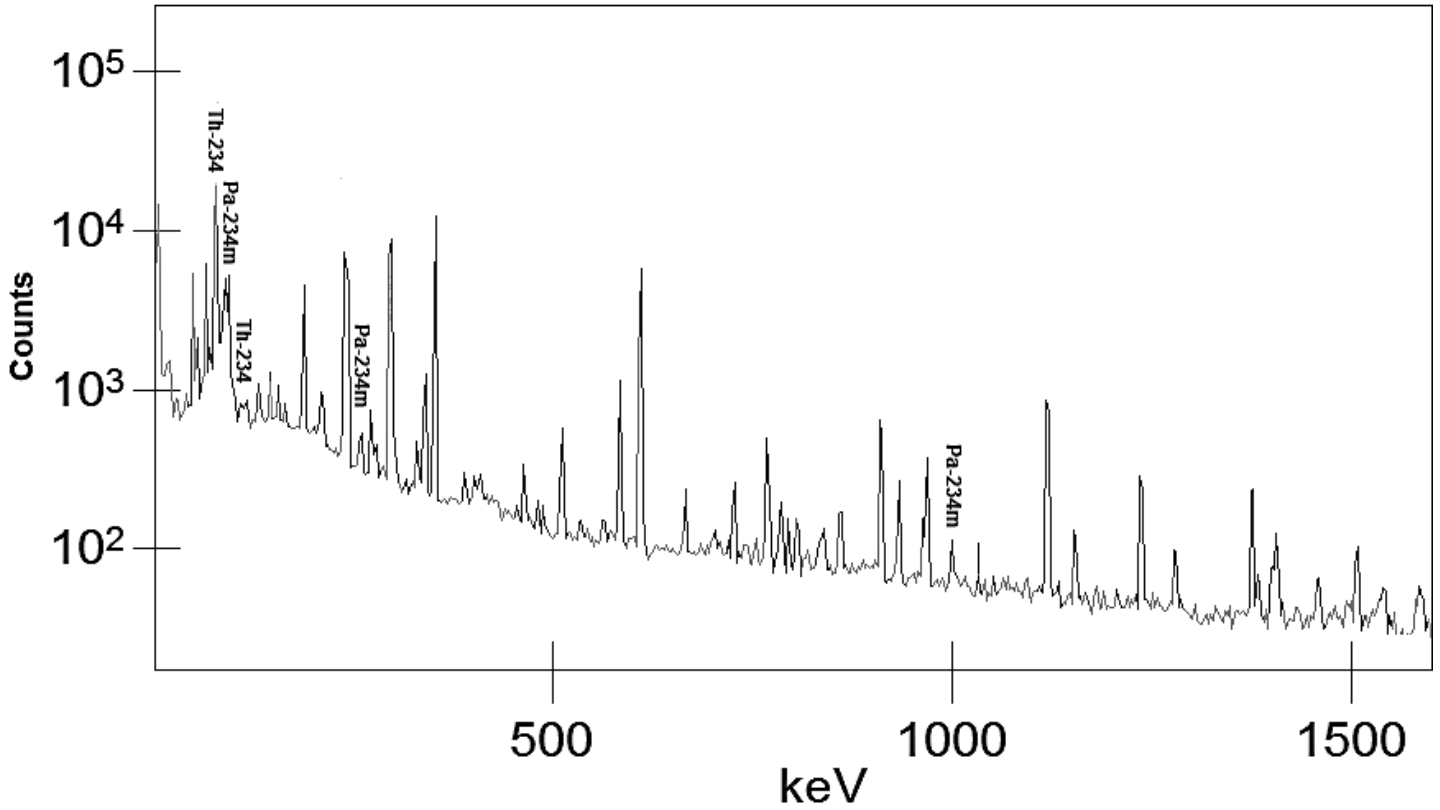

Figure A.5. Spectra of ^{234}Th (63 and 112 keV) and ^{234m}Pa (98, 258 and 1001 keV) gamma emission peaks identified as an indicator of significant ^{238}U activity in a fertiliser sample.